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SYNTHESIS AND PROPERTIES OF ANIONICALLY

GRAPHED THERMOPLASTIC ELASTOMERS

by

JOHN ARMSTRONG YOUNG

Supervisor: DR. K.E. WETTON

A doctoral thesis submitted in partial fulfilment of the
requirements for the award of the Degree of Doctor of Philosophy
of Loughborough University of Technology.

January 1981

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I would like to thank Dr. R.E. Wetton for his supervision, help and encouragement throughout this project.

Thanks are also due to Professor K.W. Bentley for the use of laboratory facilities and to the Hepworth Iron Company Ltd. for their financial support. I would also like to thank Dr. J.V. Dawkins and G. Staniforth for their interest in this work and H. Coupe for his technical assistance.

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ORIGINAlITY

The work presented in this Thesis has been carried out by the author, except where otherwise acknowledged, and has not previously been submitted to this University or any other institution.
ABSTRACT

Through the use of a sec-butyllithium, N,N,N',N'-tetramethylethylene-diamine chelate complex it was possible to anionically graft a conventional unvulcanised rubber, SBR (Solprene 1204), with vinyl aromatic monomers such as styrene, α-methylstyrene and vinyltoluene. By choosing suitable solvents and reaction conditions high yields were obtained. Grafting efficiencies, determined from the amounts of homopolymer present in the gel permeation chromatograms of the products, were found in the 60 to 100% range. Grafting efficiencies for the α-methylstyrene only systems were generally found at the lower end of this range whereas the grafting efficiencies for the other SBR graft copolymers were usually greater than 90%. Possible reasons for these differences are discussed.

Characterisation of the graft copolymers, in terms of molecular weight and composition, was carried out using gel permeation chromatography, membrane osmometry and nuclear magnetic resonance techniques. Because it was found, via ozonolysis and gel permeation chromatography, that graft molecular weight was the same as that of the homopolymer produced as a result of inefficient grafting, the presence of this latter species in the products was used as a means for readily determining the molecular weight characteristics of the grafts. The number of grafts per polymer chain was calculated from the amount of 'active' initiator added.

Dynamic mechanical studies of moulded and solvent cast samples of the SBR graft copolymers have shown that a phase separated structure exists. The position and shape of the high temperature tan δ damping peak did, however, suggest that the hard phase was a mixed phase containing a small amount of SBR. The ultimate properties of the graft copolymers were comparable with those of vulcanised SBR. Compression set values, measured under standard conditions, were poor compared to conventional vulcanisates.
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INTRODUCTION

The continued growth in rubber usage has led in recent years to the development of a new group of rubbers called 'thermoplastic elastomers'. These materials are unique in that no curing or vulcanisation process is required. Crosslinking is achieved by a physical, as opposed to a chemical, process. At ambient temperatures these physical crosslinks are permanent but at elevated temperatures break down and allow the material to be processed like a thermoplastic. On cooling the crosslinks reform and the material exhibits elastomeric properties. This reversible process enables the recycling of excess or waste material, something which is not possible with a conventional thermoset elastomer.

There are several ways in which the labile crosslinking process can be achieved and these are highlighted by the four major types of thermoplastic elastomers available commercially, i.e., ABA block copolymer, polyester, polyurethane and polyolefin thermoplastic elastomers.

The most well known of the ABA type polymers are the polystyrene-\(\alpha\)-polydiene-\(\omega\)-polystyrene block copolymers (1-3). The incompatibility of the two polymers causes phase separation to occur (see section 2.7). At low volume fractions the polystyrene exists as discrete spherical glassy (hard) domains attached to a matrix of (soft) elastomeric polydiene chains (4). It is these domains acting as anchoring points for the polydiene which enables the material to behave as a crosslinked elastomeric system.

The polyester thermoplastic elastomers are block copolymers composed of alternating crystalline (hard) and amorphous (soft) segments (5).
They are prepared by a simple ester interchange reaction between, for example, a polytetramethylene ether glycol, 1,4-butanediol and dimethyl terephthalate. This produces long chains containing crystalline regions of random length polyester blocks with the glycol blocks forming the amorphous phase. The crystalline regions form crystallites which act as network junctions for the amorphous, rubbery chains.

The polyurethane thermoplastic elastomers are also block copolymers of hard and soft segments made by the copolymerisation of a diisocyanate with a mixture of 1,4-butanediol and a poly(tetramethylene adipate) glycol (6). A linear polymer is produced with short amorphous polyester blocks and hard 'paracrystalline' (7) polyurethane blocks. The latter form the hard domains which act as the network junctions for the rubbery polyester blocks.

The polyolefin group although encompassing a wide range of thermoplastic elastomers are generally considered as mechanical blends of an ethylene-propylene-diene monomer rubber (EPDM) and a thermoplastic such as polypropylene or polyethylene. The morphology of these blends suggests an EPDM matrix reinforced with tiny polypropylene spherulites (8). A fraction of the EPDM chain crystallises in surface regions of neighbouring polypropylene spherulites tying them together in an essentially crosslinked system. On heating the spherulites break down and the rubber can then be processed like a normal thermoplastic.

Although there are other groups of materials which can be regarded as thermoplastic elastomers (9), the aforementioned types represent the main commercial thermoplastic elastomers on the market today and are used in the manufacture of such things as adhesives, coatings, automotive parts, shoe soles and various sports goods. They are, however, considered unsuitable in critical engineering applications.
The purpose of this project was to investigate the possibility of producing a thermoplastic elastomer with tensile and compressive properties comparable to a vulcanised rubber in the mid hardness range. The polyolefin, ester and urethane thermoplastic elastomers all have high hardness values. Softer materials can be achieved by blending, but to the detriment of the physical properties.

The ABA block copolymers show the greatest potential in meeting stringent requirements. They are synthesised by a homogeneous, termination controlled anionic (living) polymerisation method (10) which enables an endless variety of block copolymers to be produced, with precisely controlled molecular weights and composition (11) and subsequently, control over physical properties. The potential, commercially, of such procedures is reflected in the many patents which cover the use of different monomers, molecular weight ranges, polymerisation procedures, experimental conditions and copolymer sequences (12, 13). In addition to the linear ABA type structure other block copolymer thermoplastic elastomers have been prepared with a branch like structure, these include graft copolymers and commercially available star or radial block copolymers (14). The graft copolymers are of particular interest because they can be prepared by directly grafting suitable monomers onto conventional unvulcanised rubbers using anionic grafting techniques (15, 16). Thermoplastic elastomeric graft copolymers have been prepared by cationic methods (17), however it is often necessary to chemically modify the backbone polymer prior to the in situ operations of site initiation and graft polymerisation.

The present work has been concerned with the anionic grafting of several rubbers with vinyl aromatic compounds using a sec-butyllithium (s-BuLi), N,N,N',N'-tetramethylethylenediamine (TMEDA) initiator system.
Initial studies were carried out on the grafting of polyisoprene with styrene or α-methylstyrene to investigate the reported (15, 18) high efficiencies for these systems and also to evaluate the effectiveness of the experimental techniques used. To prevent premature termination by reactive impurities, anionic polymerisations must be carried out under rigorous experimental conditions (19), this can be achieved by performing all drying and polymerisation operations under vacuum, inert gas or dry nitrogen. The use of high vacuum and nitrogen conditions for drying the reagents and argon and nitrogen blanket methods for carrying out the grafting reactions, have been investigated.

Two commercial unvulcanised rubbers, EPDM and styrene-butadiene-rubber (SBR), were chosen as suitable backbone polymers on which to graft various monomers. The grafting of EPDM with styrene was attempted. Graft copolymers of SBR and styrene, α-methylstyrene, a styrene/α-methylstyrene mixture and vinyltoluene were prepared. Using SBR grafted with styrene and/or α-methylstyrene as model systems the effects of various experimental conditions, solvents and quantities of reagents used, on the polymer products have been investigated. Several homopolymers of styrene and α-methylstyrene were prepared for comparison.

The physical properties of several graft copolymers suitable for solvent casting or moulding have been evaluated. It has been shown by Karoly (20) and Fetters and Morton (21) that the replacement of styrene with α-methylstyrene in ABA thermoplastic elastomers produces materials with high softening points, the extent of this effect in the graft copolymers mentioned above has been investigated. It was, therefore, the intention of the present work to produce a thermoplastic elastomer suitable for an engineering application and with a high use temperature (＞100°C) by the incorporation of α-methylstyrene into the SBR graft copolymer structure.
2.1 ANIONIC POLYMERISATION

2.1.1 Initiation

Initiation of anionic polymerisations can be achieved using aromatic complexes of alkali metals, alkali metals or organolithium compounds. The mechanisms associated with each of these methods are outlined below.

**Initiation by Aromatic Complexes of Alkali Metals**

It was found by Scott (22) that styrene and dienes could be very easily polymerised by the greenish blue solutions formed by the reaction of sodium with naphthalene in dimethoxyethane. The structure of the initiator complex, later determined by electron spin resonance (23), was found to be monomeric radical anions possessing an extra electron in the lowest unoccupied \( \Pi \) orbital. Their formation is a function of both the solvent and aromatic hydrocarbon. The solvent aids in the transfer of an electron from the sodium to the naphthalene and then stabilises the complex by interorbital exchanges with available electrons, e.g. from the oxygen of the ether solvent. Using tetrahydrofuran (THF) as the solvent it can be shown thus,

\[
[\text{C}]+\text{Na}^+ + \text{THF} \quad \Rightarrow \quad \left[\text{C[O]}\right]^+_{2} \text{Na}^+ \text{(THF)}
\]  

(2.1)

It was shown by Szwarc (24) that the initiation of the styrene polymerisation was accomplished by an electron transfer process, the following mechanism being proposed:
The sodium naphthalene complex transfers its charge to the styrene to produce a radical anion which very quickly dimerises to produce a dianion. This is then capable of polymerising the styrene from each of its anionic sites. For one end:

\[
\begin{align*}
2 \left[ \text{CH}_2=\text{CH}_2 \right]^{2-} \text{Na}^+ & \rightarrow \overset{\text{Na}^+}{\text{Na}^+} \text{CH}_2=\text{CH}_2 \text{CH}_2=\text{CH}^+ \text{Na} \\
\left[ \text{CH}_2=\text{CH}_2 \right]^{2-} \text{Na}^+ \rightarrow \overset{\text{Na}^+}{\text{Na}^+} \text{CH}_2=\text{CH}_2 \text{CH}_2=\text{CH}^+ \text{Na} & \rightarrow \overset{\text{Na}^+}{\text{Na}^+} \text{CH}_2=\text{CH}_2 \text{CH}_2=\text{CH}^+ \text{Na}
\end{align*}
\]

(2.3)

Substituting a diene for styrene follows the same basic anionic mechanism.

**Initiation by Alkali Metals**

Stavely (25) found high cis-1,4-polyisoprene could be synthesised using a lithium metal catalyst. The development of a system for producing a polymer very close to that of natural rubber created a great deal of interest and it was found that initiation involved an electron transfer process similar to that of the sodium naphthalene system.

In the lithium-initiated polymerisation of butadiene Zeigler (26) suggested a mechanism involving electron transfer steps as the result of a monomeric disodium adduct being present:

\[
\text{Li} + \text{CH}_2=\text{CH}=\text{CH}_2 \rightarrow \overset{\text{CH}_2=\text{CH}=\text{CH}_2 \text{Li}^+}{\text{CH}_2=\text{CH}=\text{CH}_2 \text{Li}^+}
\]

(2.5)
\[2\text{CH}_2-\text{CH}=\text{CH}-\text{CH}_2\text{Li}^+ \rightarrow \text{Li}^+\text{CH}_2-\text{CH}=\text{CH}-\text{CH}_2-\text{CH}=\text{CH}-\text{CH}_2\text{Li}^+ \] \hspace{1cm} (2.6)

and/or

\[\cdot\text{CH}_2-\text{CH}=\text{CH}-\text{CH}_2\text{Li}^+ + \text{Li} \rightarrow \text{Li}^+\text{CH}_2-\text{CH}=\text{CH}-\text{CH}_2\text{Li}^+ \] \hspace{1cm} (2.7)

**Initiation by Organolithium Compounds**

These initiators are soluble in a variety of non-polar as well as polar solvents. They are the most widely used initiator systems because of the large number of monomers that can be used. They function by direct anionic attack rather than electron transfer, e.g. n-butyl lithium (n-BuLi) with styrene,

\[\text{n-BuLi} + \text{CH}_2=\text{CH} \rightarrow \text{n-BuCH}_2-\text{CH}_2\text{Li}^+ \] \hspace{1cm} (2.8)

Because we are dealing with charged species, the solvent has a strong influence on the initiation reaction. Polar solvents encourage the formation of free ions whereas non-polar solvents tend to give contact ion-pairs.

\[\text{increasing solvent polarity} \quad \text{contact ion pair} \quad \text{solvent separated pair} \quad \text{free ions} \] \hspace{1cm} (2.9)

In hydrocarbon media the reaction between some organolithium compounds and dienes and styrene is very slow. This is partially attributed to the aggregation of the organolithium species into dimers and higher associates depending on the type of initiator and solvent used. n-BuLi exists as hexamers in benzene and cyclohexane (27) whereas s-BuLi exists as tetramers (28) in these solvents. It was originally assumed that initiation with n-BuLi proceeded only with the unassociated species, giving a one-sixth order dependence of initiator rate on initiator concentration. However,
kinetic studies obtained for the initiation of styrene in cyclohexane and benzene using n-BuLi have indicated an initiation reaction order of between one-sixth and first-order (29, 30). Further work using other organolithium initiators for styrene and dienes in various solvents confirmed that there was not a direct relationship between association state and reaction order (28).

It was suggested by Brown (31) that initiation by the associated form could also occur. The determination of an initiation mechanism is further complicated by the fact that self-and cross-associations between initiator and living polymer may also take place.

Although the kinetics of initiation are not fully understood some assumptions can be made about the relative reactivities of various alkyl-lithium species with styrene and dienes in hydrocarbon solvents (32, 33). For a given solvent the rate of initiation for diene monomers is in the order:

\[
s-\text{BuLi} > \text{iso-PrLi} > t-\text{BuLi} > n-\text{BuLi} \text{ and } \text{EtLi} \]

For styrene it is:

\[
s-\text{BuLi} > \text{iso-PrLi} > t-\text{BuLi} \text{ and } \text{EtLi} > t-\text{BuLi} \]

For a given initiator the rates of initiation in several solvents are in the order:

\[
toluene > benzene > n\text{-hexane} > \text{cyclohexane} \]

Except for t-BuLi the relative reactivities of the initiators towards dienes and styrene are identical. The slow initiation of styrene with t-BuLi was initially attributed to steric hindrance effects (34), however it was later noted that there was an initial rapid reaction between styrene and a fraction of the initiator followed by a gradual decrease in rate (35). This produced a low molecular weight tail in the molecular weight distribution of the resulting polymer. It was suggested by Morton and Fetters (36) that two initiator species are present, t-BuLi self-
associated and t-BuLi cross-associated with polystyryllithium and each having different reactivities towards styrene. From the relative reactivities given above it can be seen that s-BuLi is a more reactive initiator than n-BuLi, however, the latter is still the preferred initiator for commercial applications because of its greater stability over longer periods of time.

In a similar way to polar solvents, small amounts of polar materials added to hydrocarbon solvents can affect initiator species with some interesting results. Increased initiator activity has been noticed when small amounts of THF, dioxane, pyridine, tertiary amines and quaternary ammonium salts are added to hydrocarbon systems. A review by Janes (12) contains several references relating to these initiator systems. The use of TMEDA with n-BuLi produces a very powerful 1:1 anionic initiator complex (37) having the structure:

![Structure](image)

The enhanced reactivity was attributed to the increased ionic character of the carbon-lithium bond and to the absence of associations of the n-BuLi. Replacing n-BuLi with s-BuLi produces an initiator species of even greater reactivity. The use of n- or s-BuLi, TMEDA initiator system has found applications in ethylene polymerisation (37, 38) and as a metalating agent in anionic grafting (see section 2.2.3).

2.1.2 Propagation

From kinetic studies of the polymerisation of dienes and styrene in hydrocarbon and ether (polar) solvents the propagation reaction was found
to be first-order with respect to monomer concentration ([M]) as defined by Szwarz (39)

\[- \frac{d[M]}{dt} = k_1[M] \tag{2.10}\]

where \(k_1\) is the pseudo first-order rate constant. We would also expect the reaction order to be directly proportional to the number of chain ends, i.e., initiator concentration. For the organolithium polymerisation of isoprene and butadiene in ethers or amines (40-42) the propagation reaction shows a first-order dependence on the concentration of growing chains therefore the propagation rate \((R_p)\) can be given by

\[R_p = - \frac{d[M]}{dt} = k_2[LE][M] \tag{2.11}\]

where \([LE]\) is the concentration of 'living ends' and \(k_2\) the apparent bimolecular propagation rate constant. This suggests that the active chain end species is in one form, e.g., an ion pair.

For the polymerisation of styrene in ether solvents a rate greater than one half-order and less than first-order is obtained (43). The behaviour was rationalised by proposing the simultaneous activity of both ion pairs and free ions, taking polystyryllithium \((\sim M^-Li^+)\) as an example,

\[
\begin{align*}
\sim M^-Li^+ + M &\rightarrow \sim M^-Li^+ \quad (n+1)mer \\
\sim M^- &+ M \rightarrow \sim M^- \quad (n+1)mer
\end{align*}
\tag{2.12}\]

\[
\begin{align*}
k^+ \\
k^-
\end{align*}
\tag{2.13}\]

where \(k^+\) and \(k^-\) are the propagation rate constants for ion pairs \((\sim M^-Li^+)\) and free ions \((\sim M^-)\). We can then express \(k_2\) as
where $\gamma$ is the mole fraction of free ions. For the equilibrium

$$\sim M^-Li^+ \rightleftharpoons \sim M^- + Li^+$$

The dissociation constant for the ion pairs ($K_I$) is given by

$$K_I = \frac{\gamma^2[LE]}{(1 - \gamma)}$$

For $\gamma \ll 1$, as suggested by Szwarc (44), the approximation $\gamma = (K_I)^{\frac{1}{2}}[LE]^{-\frac{1}{2}}$ is valid, and then

$$k_2 = k^+ + (k^- - k^+)(K_I)^{\frac{1}{2}}[LE]^{-\frac{1}{2}}$$

Linear plots of $k_2$ against $1/[LE]^2$ have confirmed this (45). The determination of $K_I$ by conductometric techniques (45) has shown that $k^- \gg k^+$ in many ethereal solvents. Therefore although free ions are present in relatively small amounts they are much more reactive than the corresponding ion pairs.

In hydrocarbon solvents dienes and styrene are not expected to form free ions and a first-order reaction rate with respect to living end concentration would be expected. This is not however the case, the propagation rate for styrene in benzene, toluene and cyclohexane (46, 47) was found to be one half-order in each case. Worsfold and Bywater (29) accounted for this by suggesting dimerisation of polystyryllithium occurred and that propagation proceeded only through the unassociated form:

$$2\sim M^-Li^+ \rightleftharpoons 2\sim M^-Li^+$$
\[ \sim \sim M^- Li^+ \xrightarrow{\text{n-mer}} M \xrightarrow{\text{(n+1)mer}} \sim \sim M^- Li^+ \]  

\[ k_p \]  

(2.19)

where \( K_D \) is the dissociation constant of the polystyryllithium dimers and \( k_p \) is the bimolecular propagation rate constant. The propagation rate can then be shown to be proportional to the square root of the total polystyryllithium concentration \( (\sim \sim M^- Li^+_\text{TOT}) \) by the following expression

\[ R_p = K_p K_D^{1/2} \left( \frac{\sim \sim M^- Li^+_\text{TOT}}{2} \right)^{1/2} \]  

(2.20)

This expression only applies to the polymerisation proceeding after complete consumption of initiator. It is also assumed that the unassociated ion pairs are the sole reactive species and represent only a very small fraction of the total ion concentration.

Fractional reaction orders for butadiene and isoprene in hydrocarbon solvents obtained for the expression (48)

\[ R_p = k_2 [LE]^n[M]^{1.0} \]  

(2.21)

were taken to represent association numbers of \( 1/n \). Morton and Fetters (49) have summarized the results obtained by several workers, and found that in many cases \( n = 0.17 \) or \( 0.25 \). The existence of hexamers and tetramers was however disputed after evidence from light scattering (50) and solution viscosity (35) measurements indicated only dimeric association states were present. Although equation (2.20) seems to satisfactorily explain the propagation kinetics for styrene in hydrocarbon solvents, the kinetics of propagation for dienes are not directly related to the association state. Other factors such as the possible formation of intermediate complexes between monomer and growing polymer must also have to be considered before a suitable rate equation can be derived. Fetters and
Young (51) have recently suggested that there is also no direct relationship between association state and reaction order for the case of styrene polymerisation. Their argument was based on the fact that the addition of aromatic ethers to polystyryllithium in benzene significantly affected the association state, yet kinetic data obtained by other workers (52-54) showed a constant one-half order dependence on living polymer concentration in mixed polar/non-polar solvent systems of varying composition.

Anionic polymerisations are unusual in that given the right experimental conditions there are no termination and transfer processes. These 'living' polymers (10) will continue to grow until all the monomer is depleted and because the chain end will still be reactive, polymerisation will continue when more monomer is added. If the initiation process is fast compared to propagation all the polymer chains will grow at the same rate producing a polymer with a small range of molecular weight values. Flory (118) predicted a molecular weight distribution approaching that of a Poisson distribution (see section 2.3.1)

For monofunctional initiation the number average chain length ($\bar{X}_n$) is given by the simple expression:

$$\bar{X}_n = \frac{[M]}{[I]}$$

(2.22)

where $[M]$ and $[I]$ are monomer and initiator concentrations, respectively.

For dianionic initiators (e.g. sodium naphthalene):

$$\bar{X}_n = \frac{2[M]}{[I]}$$

(2.23)

Chain transfer, although uncommon in anionic polymerisations, can occur under certain conditions. Low molecular weight chains have been found (38) in the polymerisation of ethylene using a n-BuLi,TMEDA complex
in benzene. The TMEDA promotes chain transfer between primary carbanion and benzene. Changing the solvent to n-hexane (55) eliminates this reaction. Toluene is another solvent which is known to participate in chain transfer. The organosodium initiation of styrene in toluene produces low molecular weight material (56). This transmetalation reaction involving toluene has been exploited commercially for the preparation of low molecular weight polydienes of various microstructures (57, 58).

2.1.3 Termination

Because of the reactivity of the living polymer, termination can be achieved simply by adding materials with replaceable hydrogen, e.g. water, methanol. However, the termination process can be utilised to incorporate functional groups into the polymer by the addition of suitable terminating agents. The addition of such functional groups as -OH and -COOH to various polymers has been reviewed by Fetters (59). Adding functional groups is useful in two ways, firstly the terminated polymer can take part in various post polymerisation reactions to produce larger chains and networks, and secondly the concentration and position (in grafted polymers) of active sites can be determined by introducing functional groups which can be analysed spectroscopically.

Termination with carbon dioxide, if not present in excess, leads to small quantities of coupled polymer (60),

$$RLi + CO_2 \rightarrow RCO_2Li \xrightarrow{H^+} RCO_2H$$

$$RLi \rightarrow RCO_2Li \xrightarrow{H^+} RCO_2H$$

(2.24)

$$R\ce{\nC\backslash\n} Li \xrightarrow{H^+} RCO\backslash\nOLi \rightarrow RCOR$$

(2.25)
2.1.4 Diene Microstructure

Anionic polymerisation, although having little or no control over the tacticity of the asymmetric carbon atom, does have an influence on the relative amounts of geometric isomers present in diene polymerisation. Infrared and nuclear magnetic resonance (NMR) studies have shown that for alkali metal initiators the proportion of 1,4 chain units is highest for lithium and decreases with increasing electropositive character of the alkali metal. Polar solvents (e.g. ethers, amines) increase the vinyl content of the polymer, especially with lithium. From table 2.1 it can be seen that for polyisoprene prepared in THF the microstructure is predominantly made up of 3,4 and 1,2 addition units whereas in hydrocarbon solvent 70 to 80% of the units are cis-1,4. A similar effect is found with butadiene which has a high (>90%) 1,4 content when prepared in hydrocarbon solvent while ethers convert the structure to a high vinyl content. The above observations have been attributed to the degree of ionic character in the metal-carbon bond at the propagation end. From NMR data which suggested the existence of σ- and π bonded lithium, Morton and Fett5 (36) proposed a mechanism to account for the effect of solvent on chain microstructure of polybutadiene. The 1,4 units were considered to result from a concerted four centre reaction between the incoming monomer and the σ bonded carbon-lithium bond, while the 1,2 units resulted from the attack by the incoming monomer at the carbon atom from the chain end, which was bonded to the lithium via a π allyl structure. A similar mechanism was proposed for polyisoprene. Polydienes with high 3,4 and 1,2 content have high glass transition temperatures and poor tensile properties, because of this anionic polymerisations of dienes are normally carried out in hydrocarbon solvents.
<table>
<thead>
<tr>
<th>Initiator</th>
<th>Solvent</th>
<th>Polyisoprene</th>
<th>Structure (%)</th>
<th>Polymerisation temperature (°C)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>t- and s-BuLi</td>
<td>Benzene</td>
<td>Polyisoprene</td>
<td>cis-1,4</td>
<td>trans-1,4</td>
<td>1,2</td>
</tr>
<tr>
<td>n-BuLi</td>
<td>Cyclohexane</td>
<td>71</td>
<td>23</td>
<td>-</td>
<td>6</td>
</tr>
<tr>
<td>t-BuLi</td>
<td>n-Hexane</td>
<td>80</td>
<td>15</td>
<td>-</td>
<td>5</td>
</tr>
<tr>
<td>t-BuLi</td>
<td>THF</td>
<td>-</td>
<td>24</td>
<td>-</td>
<td>6</td>
</tr>
<tr>
<td>n-BuLi</td>
<td>n-Hexane</td>
<td>70</td>
<td>24</td>
<td>-</td>
<td>6</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Polybutadiene</td>
<td></td>
</tr>
<tr>
<td>n-BuLi</td>
<td>n-Hexane</td>
<td>35</td>
<td>57</td>
<td>8</td>
<td>-</td>
</tr>
</tbody>
</table>
2.1.5 Copolymerisation of Dienes and Styrene

For the copolymerisation of styrene and dienes in hydrocarbon or polar solvents using alkyllithium initiation the following reactions can take place:

\[
\begin{align*}
&\text{\textcircled{11}} \quad \text{SS}^-\text{Li}^+ + S \xrightarrow{k_{11}} \text{SS}^-\text{Li}^+ \\
&\text{\textcircled{12}} \quad \text{SD}^-\text{Li}^+ + D \xrightarrow{k_{12}} \text{SD}^-\text{Li}^+ \\
&\text{\textcircled{21}} \quad \text{DD}^-\text{Li}^+ + S \xrightarrow{k_{21}} \text{DD}^-\text{Li}^+ \\
&\text{\textcircled{22}} \quad \text{DD}^-\text{Li}^+ + D \xrightarrow{k_{22}} \text{DD}^-\text{Li}^+ 
\end{align*}
\]

In a hydrocarbon solvent reaction (2.26) predominates almost to the total exclusion of styrene. It is only when the diene becomes depleted that styrene begins to polymerise and then at a rate faster than that of the diene. Adding small amounts of ethers or amines can drastically change the situation, and we get the styrene polymerising preferentially to the diene, equation (2.26). This emphasises the role the solvent plays in determining the ionic character of the growing species. Solvents having atoms with unshared electron pairs can exert a pronounced solvating effect on the cations and thus alter the structure of the ion pair. This solvation of the ion pair manifests itself in two ways: incorporation of styrene into the copolymer chain is enhanced, and the vinyl mode of addition of the diene units is increased (see section 2.1.4).

The reversal of reactivity of styrene and dienes in copolymerisation in a pure hydrocarbon solvent has been partially attributed, on kinetic grounds, to a crossover reaction between polystyryllithium and a diene, reaction (2.27), which is fast compared to the other three propagating
steps. Rate constants for the crossover reactions can be obtained spectroscopically as a result of the absorption differences in the visible and ultraviolet region between polystyryllithium and polydienyllithium. Reaction (2.27) goes from red to colourless and reaction (2.29) goes from colourless to red. Crossover rate constants obtained in this way for styrene and butadiene in cyclohexane (65) have been compared with the homopolymerisation rate constants to obtain values for $r_1$ and $r_2$, the reactivity ratios for styrene and butadiene respectively, where $r_1 = k_{11}/k_{12}$ and $r_2 = k_{22}/k_{21}$. They found $r_1 \approx 0.04$ and $r_2 = 26$, the small value of $r_1$ being due to the fast crossover rate of reaction (2.27). The large differences in rate cannot be explained solely from resonance energy or steric hindrance effects. A theory was suggested by Korotkov (66) to account for the observed values in terms of the specific solvent effect exerted by the dienes. This involves the dienes 'solvating' the ion pair chain end, something which presumably the styrene cannot do. When a more powerful solvating agent is added it reduces the effective diene solvation and then allows the monomers to polymerise at their own respective rates.
2.2 ANIONIC METHODS FOR THE PREPARATION OF BLOCK, STAR AND GRAFT COPOLYMERS

Although a 'block copolymer' literally defined refers to any polymer composed of two or more dissimilar homopolymer blocks chemically bonded together and therefore includes polymers of different structures such as star or graft copolymers, the term generally only refers to linear block copolymers of the type AB, ABA or (AB)_n. See appendix for explanation of this and other nomenclature used. Much literature has been published on the subject of anionically prepared linear block copolymers and there are some excellent reviews covering the subject (11, 12, 36, 59, 67), however for brevity only those block copolymers with an ABA structure and in particular those with thermoplastic elastomeric characteristics will be discussed here. Similarly, only star block copolymers with an (AB)_nX structure exhibiting thermoplastic elastomeric properties are considered. The general methods for preparing graft copolymers (BgA) are considered with emphasis being given to those with thermoplastic elastomeric properties.

2.2.1 Linear Block Copolymers

The preparation of ABA type copolymers by anionic means can be achieved in several ways using mono- and difunctional initiators (68) and these are outlined below;

Three stage process using monofunctional initiation

Taking a typical ABA polystyrene-b-polybutadiene-b-polystyrene (abbreviated to styrene-butadiene-styrene) polymerisation as an example, the styrene is polymerised first using a BuLi initiator in hydrocarbon solvent. The slow initiation step due to the associations of the BuLi in hydrocarbon solvent can be speeded up by the addition of small amounts of anisole or aniline to the solution in concentrations 5 to 10 times the
concentration of initiator (69). These promoters do not affect the diene microstructure (70-72).

A slow initiation reaction compared to propagation could mean residual initiator still being present upon depletion of styrene monomer, leading to a polymer with a higher molecular weight and broader distribution than anticipated. To attain optimum mechanical properties the polystyrene must be in the 10,000 to 15,000 molecular weight range (72). The presence of low molecular weight material can have a profound effect on the glass transition temperature ($T_g$), it has been shown that $T_g$ increases rapidly with molecular weight up to number average molecular weights of 10,000 (73). Therefore upon heating the lowest molecular weight polystyrene segments would soften first leading to a breakdown of the crosslinked structure. For a given molecular weight it is desirable that the polystyrene blocks are as monodisperse as possible in order to extend the temperature range over which the network structure will hold. For these reasons a fast initiation reaction for polystyrene is required.

The second stage in the preparation is the addition of the diene, the crossover reaction being almost instantaneous as indicated by the fast colour change from red to colourless. On completion of the diene polymerisation the final stage in the three part preparation is the addition of the second quantity of styrene. This crossover reaction can be speeded up by adding small quantities of THF, the diene already formed will be unaffected by this polar solvent.

This three stage sequential polymerisation method has a very limited application beyond that of styrene-diene-styrene block copolymers. A sequential method has been used (74) for the preparation of an ABA block copolymer of polystyrene or poly($\alpha$-methylstyrene) and poly(2-methyl thiabutane) with this latter polymer forming the centre ($B$) block. Another novel system prepared in this way was the elastomeric block
copolymer poly(styrene-co-1,1 diphenyl ethylene)-b-polybutadiene-b-poly (styrene-co-1,1 diphenyl ethylene) (75). The end blocks having a $T_g$ of 140°C enables these materials to have a higher use temperature than those with polystyrene end segments.

**Two stage process with difunctional initiators**

This is preferred to the previous method for ABA synthesis, because only two sequential monomer additions are carried out, B followed by A. This reduces the possibility of premature termination due to impurities present in the monomers. If termination should occur homopolymer and not diblock impurities will form, the latter being detrimental to the physical properties of the triblock copolymer (76). A further advantage of this polymerisation method is in the synthesis of an ABA block where B can initiate A but not vice versa, e.g. when B is a vinyl or diene block and A is an ethylene oxide or methacrylonitrile block (74). The disadvantage of such a system is the number of initiators only soluble in polar solvent, e.g. sodium naphthalene. When B is a diene block hydrocarbon solvents are required. Lithium metal could be used to produce a high 1,4 structure but the extremely slow initiation rate of such heterogeneous systems makes it impossible to control the molecular weight within the limits required, e.g. 50,000 to 100,000 (72). Dilithium initiators have been prepared (21) in hydrocarbon solvent in the presence of small amounts of aromatic ethers which do not affect the diene microstructure.

The synthesis of ABA block copolymers of polystyrene or poly($\alpha$-methylstyrene) and polyisoprene in which the latter forms the centre block represent the only successful examples of thermoplastic elastomers prepared by dianionic initiation.
Monofunctional initiation and coupling

As with the difunctional initiators only two monomer additions are required, A followed by B and then the two chains joined by a suitable coupling agent (X) to give AB-X-BA which is effectively an ABA type polymer. This method can be used when A will initiate B and not vice versa, e.g. the preparation of an ABA block copolymer where poly(propylene sulphide) is the centre block and polystyrene or poly(α-methyl styrene) the outer blocks (77).

Efficiency in coupling systems must be high to ensure the presence of uncoupled diblock material is kept to a minimum. G.p.c. analysis (78) of some commercial styrene-diene-styrene block copolymers has shown the presence of diblock material due either to an incomplete coupling reaction or as a result of an intentional premature termination step.

Dihalogen compounds are often used for the coupling reactions (79,80):

\[ 2\text{ABLi} + \text{XXY} \rightarrow \text{ABXBA} + 2\text{LiY} \quad (2.30) \]

A side reaction which may occur is substitution instead of elimination and coupling:

\[ 2\text{ABLi} + \text{XXY} \rightarrow 2\text{ABY} + \text{LiXY} \quad (2.31) \]

Phosgene has been used as the linking agent for the copolymerisation of isoprene and 4-vinyl biphenyl (81) and also for the preparation of an ABA block copolymer of α-methylstyrene and propylene sulphide (77, 82).
Two stage process using monofunctional initiation and tapering

This method relies on the different reactivities of the monomers, to produce blocks when both monomers are present. In the preparation of styrene-butadiene-styrene the styrene is polymerised first, then a mixture of styrene and butadiene is added. Any termination at this stage will lead only to homopolymer. Immediately the butadiene is added the crossover reaction from polystyryllithium to polydienyllithium occurs and the butadiene then polymerises preferentially until almost depleted and then the styrene starts to polymerise. The changeover from diene to styrene is not sudden and a small section of polymer is random in nature - gradually decreasing in butadiene and increasing in styrene. This tapered section, because of its random nature, shows poor incompatibility and some phase mixing occurs. This leads to poor tensile properties, and it is therefore advantageous to have a tapered section as small as possible. The poorer physical properties of styrene-isoprene-styrene compared to styrene-butadiene-styrene prepared in this way have been attributed to the greater proportion of random polymer present in the former polymer (83).

This procedure, utilising the reactivity differences of the two monomers, can be applied to difunctional initiation where only a one stage initiation process is employed. A major disadvantage of this method is the production of diblock material if impurity termination occurs. The diene which polymerises first can be combined with other styrene type monomer such as $\alpha$-methylstyrene, $\alpha$-vinylnaphthalene, 4-vinylbiphenyl and 1,2-dihydronaphthalene (74). The use of $\alpha$-methyl styrene in such a method shows good incompatibility with the diene and little or no tapered block is formed.
2.2.2 *Star Block Copolymers*

In the same way that coupling agents can be used to join two polymers together to form an ABA block copolymer, linking agents with a functionality of three or more can be used to prepare star or radial block copolymers. Linking agents were first used to prepare tri- and tetra-chain polystyrenes (84). This was later extended to the commercial preparation of styrene and butadiene (or isoprene) block copolymers with a functionality of four (85). Analysis of these commercial materials by g.p.c. (49) has shown little or no unlinked material to be present, indicating the use of a very efficient linking agent. The efficiency of the linking reaction is a function of both the living polymer and the linking agent itself. Silicon tetrachloride reacted with polyisoprenyllithium (35) and polystyryllithium (84) produces a mixture of tri- and tetra-chain material whereas with polybutadienyllithium (86) only tetra-chain material forms. The bulky methyl and phenyl groups therefore prevent a complete reaction with the linking agent.

In addition to the elastomeric tri- and tetra-chain block copolymers that have been prepared (85, 87-89), multi arm block copolymers of styrene and dienes with a functionality of 6 to 30 have been synthesized using divinylbenzene as a linking agent (89, 90).

2.2.3 *Anionic Graft Copolymers*

The many routes to anionic graft copolymers have been reviewed by several authors (67, 91-93). They can be prepared using either 'grafting onto' or 'grafting from' techniques.

In 'grafting onto' a backbone polymer containing functional groups along the chain can be used to deactivate living polymer chains, whereupon these chains become the grafts, e.g. the grafting of living polystyrene onto poly(methylmethacrylate) (94), poly(vinylchloride) (95), poly(iso-
butylene) (96), poly(2-vinylpyridine) (97) and a styrene-diisopropenylbenzene random copolymer (98). Other backbone polymers containing functional groups include partially chloromethylated polystyrenes (99-101) and copolymers of styrene and poly(vinylstyrene oxide) (101).

In 'grafting from' metal organic sites added to the polymer backbone can initiate the polymerisation of some monomer, thus yielding the grafts. The metalation can be achieved by metal-halogen interchange such as the reaction of brominated polystyrene with BuLi (102) and the subsequent polymerisation of a suitable monomer, e.g. acrylonitrile (103). Excess initiator is required to prevent a Wurtz-Fitting reaction, but this itself is removed prior to monomer addition to prevent homopolymer formation. Site initiation can occur by electron transfer producing radical anions (104) or by the introduction of dialkylaluminium sites to give alkyl aluminium initiators (105). Copolymers of butadiene and 2-vinylnaphthalene have been metalated with n-BuLi in THF, and the metalated copolymer used to initiate the polymerisation of styrene or 2-vinylnaphthalene (106). Materials having properties similar to styrene-butadiene-styrene block copolymers were obtained. The discovery of the powerful metalating agent n-BuLi.TMEDA introduced new possibilities with anionic grafting. It has been used successfully as the metalating agent for polystyrene (107), polyisoprene and polybutadiene (108). The grafting of vinyl monomers such as styrene onto polydiene using this complex has been carried out by several workers (109-115), however in most cases moderate to low efficiencies were encountered. Using s-BuLi instead of n-BuLi with TMEDA as the metalating agent for dienes and EPDM enabled Falk and coworkers (18) to produce thermoplastic elastomeric materials in high yields and under mild reaction conditions. Other metalating agents such as BuLi activated with potassium alkoxides have been used for grafting styrene onto EPDM (116) and a random copolymer of
styrene and butadiene onto polybutadiene (117). The catalyst efficiency was reported to be lower than that of s-BuLi.TMEDA.
2.3 MOLECULAR WEIGHT DISTRIBUTIONS OF IDEAL ANIONIC SYSTEMS

2.3.1 Homopolymers

For the ideal anionic polymerisation in which
a) all termination processes have been excluded,
b) initiation is fast compared to propagation,
c) the propagating species all grow at the same rate,
d) the concentration and temperature are uniform throughout the reaction vessel,
and e) the equilibrium strongly favours polymer,
then the resulting polymer will have a Poisson molecular weight distribution \( (118) \) with the number fraction of \( j \)-mers, \( P_j \), given by

\[
P_j = \frac{e^{-x} x^{j-1}}{(j-1)!} \tag{2.32}
\]

where \( x \) is the number of monomers reacted per initiator molecule. The weight fraction distribution is given by

\[
W_j = \left( \frac{x}{x+1} \right) e^{-x} x^{j-2} \tag{2.33}
\]

If the degree of polymerisation of the initial living polymer is assumed to be unity (a permissible simplification) then

\[
\overline{x}_n = (x + 1) \tag{2.34}
\]

and

\[
\overline{x}_w = (x + 1) + \left( \frac{x}{x+1} \right) \tag{2.35}
\]

where \( \overline{x}_w \) is the weight average degree of polymerisation. Dividing equation (2.35) by equation (2.34) we get
\[
\frac{x_n}{x} = 1 + \frac{x}{(x+1)^2} \approx 1 + (x_n)^{-1}
\]  

(2.36)

The degree of uniformity attained in polymers having a Poisson molecular weight distribution increases greatly with their size. For example, when \(x_n = 100\), about 70% by weight of the polymer is composed of chains having their molecular weights within 10% of the average value. The proportion of such chains increases to 96% for a degree of polymerisation of 500.

The ratio \(x_n/x\) for these materials are 1.01 and 1.002 respectively.

The molecular weight distribution of a polymer is generally given in terms of the polydispersity, i.e.

\[
\text{polydispersity} = \frac{\bar{M}_w}{\bar{M}_n}
\]  

(2.37)

where \(\bar{M}_w\) is the weight average molecular weight and \(\bar{M}_n\) the number average molecular weight. \(\bar{M}_w\) is defined as

\[
\bar{M}_w = \frac{\sum w_i M_i}{\sum w_i} = \frac{\sum N_i M_i^2}{\sum N_i M_i}
\]  

(2.38)

where \(w_i\) is the weight and \(N_i\) the number of molecules with molecular weight \(M_i\). \(\bar{M}_n\) is defined as

\[
\bar{M}_n = \frac{\sum N_i M_i}{\sum N_i}
\]  

(2.39)

Polymers with \(\bar{M}_w/\bar{M}_n < 1.1\) are normally regarded as being monodisperse. Many monodisperse polymers have been prepared anionically (36), these include polystyrene, poly(α-methylstyrene), polyisoprene, polybutadiene and poly(methyl methacrylate).
2.3.2 Graft Copolymers

The molecular weight distributions of anionic graft copolymers will very much depend on the synthesis method employed. Only a random 'grafting from' process will be considered here.

The first step involves the metalation of the backbone polymer. A typical example is the metalation of polystyrene or polybutadiene using n- or s-Buli in the presence of TMEDA. Although the average number of sites per backbone polymer is precisely controlled by the amount of metalation complex added, there will be a distribution of the actual number of sites on each polymer molecule. The subsequent grafting process will then produce a polymer with a molecular weight dependent on the number of grafts. To determine the effect this grafting process will have on the molecular weight distribution of the resulting polymer we must first consider the statistical distribution of the graft sites.

The probability, \( F(n) \), of finding \( n \) graft sites on a backbone molecule is given by the normal distribution

\[
F(n) = \frac{(AN)!}{n!(AN-n)!} \left( \frac{1}{N} \right) \left( 1 - \frac{1}{N} \right)^{AN-n}
\]

(2.40)

where \( A \) is the average number of graft sites per backbone molecule and \( N \) is the number of backbone molecules. When \( A \) is constant and \( N \to \infty \) equation (2.40) approaches Poisson distribution. It is assumed that the number of metalation sites available in the backbone molecule far exceeds the average number of actual sites on the subsequent metalations. The position distribution on each molecule is also regarded as being statistically independent of the other molecules. Using equation (2.40) Cha (119) has calculated the graft site distributions for \( A = 1, 2, 5 \) and 10, when \( N = 10^6 \). These are shown graphically in figure 2.1. In a real system \( N \) would be in the order of \( 10^{20} \) molecules, however Cha found
FIGURE 2.1
Graft site distribution

FIGURE 2.2
Changes in polydispersity with the number and molecular weight of the grafts
that the results were the same whether \( N = 10^6 \) or the limiting value of \( N \to \infty \). Let us now consider the case where we have a backbone polymer with \( \bar{M}_n = 100,000 \) and \( \bar{M}_w/\bar{M}_n = 1.00 \) which is grafted with a polymer having \( \bar{M}_n = 10,000 \) and \( \bar{M}_w/\bar{M}_n = 1.00 \). A graft copolymer with \( n = 1 \) will therefore have a molecular weight of 110,000, and \( n = 2 \) a molecular weight of 120,000, etc. From the frequency diagram and the total number of backbone molecules in the system \( (10^6) \) we can determine the number of molecules for each value of \( n \). For a particular value of \( A \) we can obtain \( \bar{M}_n \) and \( \bar{M}_w \) from equations (2.38) and (2.39) and hence a value for the polydispersity. Repeating the calculations for \( n = 2, 5 \) and 10 a plot of polydispersity against \( A \) can be obtained, figure 2.2. The curves for polymers with graft molecular weights of 20,000 and 30,000 are also given. From these plots it can be seen that polydispersity increases with graft molecular weight and a maximum is reached at decreasing values of \( A \) as the molecular weight of the graft increases.
2.4 GEL PERMEATION CHROMATOGRAPHY THEORY

2.4.1 Introduction

G.p.c. is an analytical technique, developed by Moore (120), for the separation of molecular species according to their size. The separation takes place in a chromatographic column filled with beads of a rigid porous gel, e.g. porous silica or highly crosslinked porous polystyrene. A sample of a dilute polymer solution is introduced into a solvent stream running through the column. Large polymer molecules are effectively excluded from the solvent present in the pores of the particles due to their large size, and are eluted from the column first. Smaller polymer molecules have access to most of the solvent inside the stationary particles and they are, therefore, eluted later than the large molecules. The molecules of intermediate size, which can partially penetrate the pores, elute at times between the two extremes. As a result, different molecular species are eluted from the column in order of their molecular size with the largest emerging first. A detector inserted in the effluent stream from the column will give a response which is proportional to the amount of polymer that is in the eluate at that time. The volume of eluent required to elute a particular species from a column, the peak (elution) retention volume \( V_R \), can be expressed in the form

\[
V_R = V_o + K_{gpc} V_1
\]  

(2.41)

where \( V_o \) is the interstitial liquid volume of the packed bed and \( V_1 \) is the volume of liquid in the pores of the packing. \( K_{gpc} \) is the experimental partition coefficient for g.p.c. with values ranging from zero for totally excluded molecules to unity for molecules which can totally permeate the pores. Many theories have been proposed to explain the mechanism that gives rise to \( K_{gpc} \) and these have been reviewed else~
where (121). They can, however, be grouped into two major types, equilibrium models and non-equilibrium models. The equilibrium models assume that the distribution of the molecules between the mobile and stationary phases is controlled by thermodynamic equilibria and so the peak retention volume of a particular species is independent of flow rate. \( K_{gpc} \) can then be represented by \( K_d \), the equilibrium distribution coefficient which results from exclusion of the solute molecules from the pores of the substrate. The non-equilibrium models relate \( K_{gpc} \) to dynamic aspects of the chromatographic process and therefore \( V_R \) will be expected to be flow rate dependent. Yau (122) expressed \( K_{gpc} \) in the form

\[
K_{gpc} = K_d K_{Di}
\]  

(2.42)

where \( K_{Di} \) is the distribution coefficient which results from the non-equilibrium process of lateral diffusion between the mobile and stationary phases. At low flow rates \( K_{Di} \) tends to unity and \( K_{gpc} \) becomes equal to \( K_d \), i.e. the distribution of solute molecules between the phases approaches the equilibrium state. Although there is no comprehensive model for g.p.c., for most operational flow rate ranges \( K_d \) can be taken as the experimental partition coefficient.

2.4.2 Calibration Procedure

Having fractionated the polymer sample with respect to molecular size it is then necessary to relate \( V_R \) values across the chromatogram to molecular weight values in order to determine \( \bar{M}_n, \bar{M}_w, M_p \) (peak maximum molecular weight) and polydispersity \( (\bar{M}_w/\bar{M}_n) \). The absence of a suitable theory to relate column character, i.e. pore structure, directly to molecular weight means a calibration procedure is required. The g.p.c. column is calibrated using narrow molecular weight distribution
samples of known molecular size or weight of the polymer under investigation. Log M values are plotted against \( V_R \). For narrow molecular weight distribution samples we can write

\[
M_p \approx R_n \approx R_w \quad (2.43)
\]

therefore differentiation between each is avoided at this stage. A typical calibration of log M versus \( V_R \) is given in figure 2.3. Three main regions of the curve may be identified:

i) A-B, where \( V_R = V_o (K_d = 0) \)

ii) B-C, where \( V_R = V_o + K_d V_i \) \((0 < K_d < 1)\)

and iii) C-D, where \( V_R = V_o + V_i \) \((K_d = 1)\)

If the region of interest B-C is linear log M and \( V_R \) are directly proportional. However, in most cases a non-linear plot is obtained and therefore calibration must be carried out over this whole molecular weight region. Having established a suitable calibration curve for a particular polymer requiring analysis it is then possible to construct a full molecular weight distribution curve for that polymer from its gel permeation chromatogram. The molecular weight distribution curve can be represented by a graph of \( \frac{dW}{dM} \) against M where \( w \) is the weight fraction of the sample with molecular weight below M. Yau (123) expressed \( \frac{dW}{dM} \) as

\[
\frac{dw}{dM} = w(M) = \frac{dw}{dV_R} \cdot \frac{dV_R}{d(\log M)} \cdot \frac{d(\log M)}{dM} \quad (2.44)
\]

Values of \( \frac{dw}{dV_R} \) are obtained from the normalised gpc chromatogram assuming detector response is directly proportional to concentration.

The term \( \frac{dV_R}{d(\log M)} \) is the reciprocal of the slope of the calibration graph and is only constant for linear calibrations. When the curve is
FIGURE 2.3
Typical g.p.c. calibration curve obtained from samples with known $M_D$ values

[Diagram showing a typical g.p.c. calibration curve with LOG M on the y-axis and DETECTOR RESPONSE on the x-axis, labeled A, B, C, and D.]

RETENTION VOLUME ($V_R$)
non-linear values of \( \frac{dV_R}{d(\log M)} \) must be calculated for each point. The last term in the equation \( \frac{d(\log M)}{dM} \) is simply \( \frac{1}{M} \). The molecular weight average can be determined using the following equations

\[
\bar{M}_n = \frac{1}{\int (1/M) \; w(M) \; dM} \tag{2.45}
\]
\[
\bar{M}_w = \int M \; w(M) \; dM \tag{2.46}
\]

For a log normal molecular weight distribution the following relationship holds (124)

\[
\bar{M}_D = (\bar{M}_n \; \bar{M}_w)^{\frac{1}{2}} \tag{2.47}
\]

2.4.3 Universal Calibration

Intrinsic viscosity ([\(\eta\)]) studies of polymer solutions have shown polymer molecules can be represented by an equivalent hydrodynamic sphere (125). The hydrodynamic volume \(V\) of the sphere can be defined by the Einstein viscosity relationship

\[
V = \frac{[\eta] M}{0.025 N_0} \tag{2.48}
\]

where \(N_0\) is the Avagadro's number and \(M\) the molecular weight. If hydrodynamic volume or a size parameter related to this volume such as the radius or diameter of the hydrodynamic sphere, controls the separation then a plot of \(\log [\eta] M\) against elution volume will be the same for all polymers. For two polymers \(A\) and \(B\) eluting at the same \(V_R\) then

\[
\log [\eta]_A \; M_B = \log [\eta]_B \; M_B \tag{2.49}
\]
If the g.p.c. column has been calibrated with standard fractions of polymer A each with a known viscosity, the molecular weight of polymer B can be determined if its intrinsic viscosity is known. This has been verified by Benoit et al. (126) for homopolymers and copolymers having various chemical and geometrical structures. The effect of solvent on the validity of equation (2.49) has been investigated for polystyrene standards and polydimethylsiloxane fractions (124). The equation was found to be satisfactory provided the solvent was a good solvent for polystyrene, i.e. \( a = 0.7 \) to \( 0.8 \), where \( a \) is an exponent in the Mark-Houwink dilute solution viscosity equation:

\[
[\eta] = K \bar{M}_v^a
\]  

where \( K \) is a constant and \( \bar{M}_v \) is the viscosity average molecular weight. If there is some knowledge of \( K \) and \( a \) for each type of polymer in the g.p.c. solvent then substituting equation (2.50) into equation (2.49) and rearranging we get

\[
\log M_A = \left( \frac{1 + a_B}{1 + a_A} \right) \log M_B + \left( \frac{1}{1 + a_A} \right) \log \frac{K_B}{K_A}
\]  

(2.51)

Values of \( K \) and \( a \) for many polymer systems are available in the literature (e.g. 127, 128), however they are only constants over a certain molecular weight range with deviations occurring in the very high and low molecular weight regions (129, 130). It is therefore often necessary to use more than one pair of \( K \) and \( a \) values.

Although Mark-Houwink constants may not be known for a polymer in a g.p.c. solvent it is often still possible to employ an approximate simple universal calibration (124) similar to equation (2.51). When the solvent is a good solvent for both polymers they very often have similar
polymer-solvent interactions and similar 'a' values. It can then be assumed that the unperturbed root-mean-square end-to-end distance \( \langle r_0^2 \rangle^{1/2} \) is the universal calibration parameter (131). Equation (2.48) was extended by Flory and Fox (132) to give

\[
[\gamma]_M = \bar{\Phi} \propto^3 \left[ \langle r_o^2 \rangle \right]^{3/2}
\]

(2.52)

where \( \bar{\Phi} \) is the universal viscosity constant and \( \propto \) represents the expansion of the polymer molecules because of polymer-solvent interactions.

For similar polymer-solvent interactions \( \propto^3 \) values are very similar and therefore \([\gamma]_M \) and \( \left[ \langle r_o^2 \rangle \right]^{3/2} \) will both be satisfactory universal calibration parameters (124, 131, 133). The \( M_A \) and \( M_B \) calibrations can then be related by

\[
\log M_B - \log M_A = \log \left[ \frac{\langle r_o^2 \rangle}{M} \right] A \left[ \frac{M}{\langle r_o^2 \rangle} \right] B
\]

(2.53)

where \( \left[ \langle r_o^2 \rangle / M \right]^{1/2} \) is a constant for a polymer and is independent of molecular weight and elution volume, values for which are available in the literature (127). For a theta solvent \( (a = 0.5) \propto \) is unity then equation (2.52) reduces to the Mark-Houwink equation

\[
[\gamma] = K_\Theta M^{1/3}
\]

(2.54)

where \( K_\Theta \) is a constant and is equal to \( \bar{\Phi} \left[ \langle r_o^2 \rangle / M \right]^{3/2} \). Equation (2.53) can then be rewritten as

\[
\log M_B - \log M_A = \frac{2}{3} \log \left( \frac{K_\Theta (A)}{K_\Theta (B)} \right)
\]

(2.55)

The above treatment for the determination of a universal calibration can be extended to block copolymers. Benoit and coworkers (134) have
suggested that the molecular dimensions of block copolymers are not
influenced by AB interactions. Consequently the dimensions of an AB
block copolymer in a theta solvent are linearly related to the dimensions
of the homopolymers by the relationship

$$\left[<r_0^2>/N\right]_{AB} = n \left[<r_0^2>/N\right]_A + (1 - n) \left[<r_0^2>/N\right]_B$$

(2.56)

where n is the weight fraction of A in the AB block copolymer. \(\left[<r_0^2>/M\right]_{AB}\)
can then be used in equation (2.53) to give (135),

$$\log M_{AB} - \log M_A = \log \left[<r_0^2>/N\right]_A \left[<r_0^2>/N\right]_{AB}$$

(2.57)

where A is the polymer for which the calibration data, \(\log M\) versus \(V_R\), is available.

The use of a universal calibration of the type given in equation
(2.49) has been used for branched polymers, i.e.

$$\log [\gamma]_L M_L = \log [\gamma]_B M_B$$

(2.58)

where the subscripts L and Br refer to linear and branched polymers,
respectively. However, several exceptions have been reported (136, and
see 137). The use of the end-to-end distance for branched polymers is no
longer a meaningful parameter when referring to polymers with more than
two ends. If we replace \(<r_0^2>\) with \(<s_0^2>\), the unperturbed mean
square radius of gyration, in equation (2.52) we obtain an expression
which then applies to all types of polymer architecture. Attempts have
been made to use \(<s_0^2>\) values to obtain an expression for a universal
calibration (136, 138), however the difficulty in producing branched
polymers with well defined structures has limited the data available to
only a few structural types, e.g. comb or star-shaped polymers. There is also a problem in choosing suitable values of $\langle s^2 \rangle / N$ because for a given molecular weight the hydrodynamic volume of the polymer decreases with increasing degree of branching.

2.4.4 Peak Broadening and Resolution

In the treatment of chromatographic separation it has been assumed that molecules of the same monodisperse polymer all elute at the same retention volume, however this is not strictly correct because for any chromatographic system axial band spreading of a sample will occur due to a variety of physical reasons. This spreading can lead to sources of error in molecular weight calculations particularly at low polydispersity values. Several workers (139-141) have compared the theoretical values of $\bar{M}_n$, $\bar{M}_w$ and polydispersity with those obtained experimentally as a means of determining column performance. Peak broadening is not however totally due to the column, there are also contributions from the sample loading device, the column fittings and the detector. Le Page (142) used a method for isolating the contribution of the column from the rest of the components. Peak broadening can be regarded as being a function of a particular chromatographic set-up and will vary from instrument to instrument even if the same column and packing are used.

Resolution ($R_s$) is defined by

$$R_s = \frac{2(V_R(B) - V_R(A))}{W_A + W_B}$$

(2.59)

where $V_R(A)$ and $V_R(B)$ are the retention volumes of A and B and $W_A$ and $W_B$ are their respective peak widths at their base. Column choice depends on the gradient of the fractionation region of the calibration graph.
(B-C in figure 2,3). The more horizontal the graph the greater the separation of the peak maximum, i.e. the greater the value of \( V_{R(B)} - V_{R(A)} \). Very often several columns of different pore size distribution are required to produce the necessary separation.
2.5 **Ozonolysis of Olefins**

The reaction of ozone with olefins is well known in organic chemistry literature and there are several specialist reviews on the subject (143, 144). The mechanism of ozonolysis of olefins (145) can be shown in the following way

\[
\text{R}_2\text{C} = \text{CR}_2 \xrightarrow{0_3} \text{R}_2\text{C} - \text{CR}_2 \xrightarrow{+ -} \text{R}_2\text{C}-\text{O}=\text{O} + \text{R}_2\text{O}=\text{O} \quad (2.60)
\]

The instability of the zwitterion formed leads to the following side reactions:

\[
\text{R}_2\text{C}-\text{O}=\text{O} + \text{R}_2\text{O}=\text{O} \xrightarrow{+ -} \text{R}_2\text{C} - \text{O}=\text{O} \xrightarrow{\text{OH}_2} \text{(ozonide)} \quad (2.61)
\]

and

\[
\text{R}_2\text{C}-\text{O}=\text{O} \xrightarrow{+ -} \text{polymeric peroxide} + \text{R}_2\text{C} - \text{O}=\text{O} \xrightarrow{\text{OH}_2} \quad (2.62)
\]

Because the purpose of the ozonolysis reaction is to break open the double bond of the olefin to form two fragments, it is necessary to stabilise the zwitterion and decompose the ozonide. This can be achieved in two ways, either by termination of the reaction at the zwitterion formation stage by reacting with a suitable compound, usually an alcohol,

\[
\text{R}_2\text{C}-\text{O}=\text{O} \xrightarrow{+ -} \text{R}-\text{OH} \xrightarrow{+ -} \text{R}_2\text{C} - \text{O}=\text{OH} \quad (2.63)
\]

and then adding a reducing agent to the hydroperoxide formed,

\[
\text{R}_2\text{C} - \text{O}=\text{OH} + (\text{CH}_3)_2\text{S} \xrightarrow{+ -} \text{C}=\text{O} + \text{ROH} + (\text{CH}_3)_2\text{SO} \quad (2.64)
\]

or by allowing the ozonisation to proceed to the ozonide stage by performing in a neutral medium, e.g. carbon tetrachloride, and then adding a reducing agent.
Typical reducing agents are palladium/hydrogen (145) and triphenylphosphine (146). Using the latter, the ozonide is converted almost quantitatively to ketones and aldehydes. It also avoids the formation of oxygen-containing by-products (147), since hydroperoxide, dimeric and polymeric peroxides and ozonides are all converted to carbonyl compounds by triphenylphosphine e.g.

\[
R_2C\overset{O}{\underset{O}{\longrightarrow}}CR_2 + RH \rightarrow 2R_2C=O + ROH
\]  

(2.65)

\[
R_2C\overset{O}{\underset{O}{\longrightarrow}}CR_2 \rightarrow R_2C=O + \overset{\circ}{\underset{\circ}{\overset{\circ}{\overset{\circ}{P}}}}_{\overset{\circ}{\underset{\circ}{\overset{\circ}{O}}}}_{\overset{\circ}{\underset{\circ}{\overset{\circ}{O}}}}
\]  

(2.66)

The products can be identified using gas-liquid chromatography methods. Ozonolysis can be used for the structural elucidation of many unsaturated organic compounds including natural and synthetic polymers. The method has been used to determine the amounts of 1,4 and 1,2(vinyl) structures in diene polymers (148, 149). The method has been further extended using 'microzonolysis' techniques to investigate head to head, tail to tail, etc. contents in some natural and synthetic rubbers (150-152). The preferred small scale techniques, carried out over short periods and at low temperatures (153), reduce the possibility of side reactions and eliminate the potential explosive characteristics inherent in large scale ozonolysis.
2.6 MECHANICAL PROPERTIES OF POLYMERS

2.6.1 Theory of Rubber Elasticity

Whereas glasses and crystalline solids have modulus values in the range $10^9$ to $10^{12}$ Pa and elastic limits less than 1%, natural and synthetic rubbers have modulus values in the $10^5$ to $10^7$ Pa range and can be reversibly stretched to several hundred per cent. The theory of rubberlike elasticity (154) is based on a model in which the chain molecules arranged at random are linked together at relatively few points to form a three-dimensional network. In the unstretched state the network chains between crosslinks are randomly coiled with $\mathcal{S}_u$ conformations, on stretching the average distance between crosslinks increases and the reduced number of conformations now available becomes $\mathcal{S}$. The change in entropy between the stretched and unstretched state is related to the number of conformations in the two states by the relation:

$$S-S_u = k \ln \frac{\mathcal{S}}{\mathcal{S}_u}$$  \hspace{1cm} (2.67)

where $k$ is the Boltzmann's constant.

Statistically the number of configurations of $\mathcal{S}_u$ and $\mathcal{S}$ can be given by:

$$S-S_u = -\frac{3}{2} N_o k (\lambda^2 + 2/\lambda - 3)$$  \hspace{1cm} (2.68)

where $N_o$ is the number of network chains and $\lambda$ the extension ratio defined as the extended length $L$ divided by the unextended length $L_u$.

From a thermodynamic treatment the extension force ($F$) is given by:

$$F = -T \left[ \frac{\partial S}{\partial L} \right]_T$$  \hspace{1cm} (2.69)
where $T$ is the absolute temperature.

Combining equations (2.68) and (2.69) we get

\[ F = \frac{N_o kT}{I_u} \left( \lambda - \frac{1}{\lambda^2} \right) \]  
\[ (2.70) \]

The tensile stress ($\sigma$) is obtained by dividing $F$ by the unstretched cross-sectional area of the sample

\[ \sigma = \frac{F}{A_u} = nRT \left( \lambda - \frac{1}{\lambda^2} \right) \]  
\[ (2.71) \]

where $R$ is the gas constant and $n$ the number of moles of network chains per unit volume and can be expressed by:

\[ n = \frac{\varrho}{M_c} \]  
\[ (2.72) \]

where $M_c$ is the number average molecular weight of the network chains and $\varrho$ is the density of the rubber.

Substituting equation (2.72) into equation (2.71) we get:

\[ \sigma = \frac{\varrho RT}{M_c} \left( \lambda - \frac{1}{\lambda^2} \right) \]  
\[ (2.73) \]

Deviations from this equation have been reported and a more general, albeit more empirical, relationship has been proposed (155) and can be written:

\[ \sigma = (2C_1 + \frac{2C_2}{\lambda})(\lambda - \frac{1}{\lambda^2}) \]  
\[ (2.74) \]

where $C_1 = \varrho RT/M_c$ and $C_2$ represents the deviation from ideal behaviour.

For low extensions ($\lambda < 4$) equation (2.74) has been shown to apply to
conventional vulcanisates (155).

2.6.2 Viscoelastic Behaviour and Definition of Terms

Polymers behave as viscoelastic bodies (156-158) exhibiting properties intermediate between perfect (Hookean) solids and perfect (Newtonian) liquids. Perfect solids obey Hooke's law where stress is proportional to strain. In perfect liquids stress is proportional to the rate of strain, Newton's viscosity law.

Under a constant stress a polymer deforms with time (creeps) and under a constant strain the stress needed to maintain the deformation is observed to decay (stress relaxation). Applying a sinusoidally oscillating stress, the strain is observed to be neither in phase (Hookean solid) nor 90° out of phase (Newtonian liquid). There are instead in phase (storing energy) and out of phase (dissipating energy) components of the resulting strain. Measurement of these properties can be carried out by creep, stress relaxation and dynamic mechanical experiments.

Creep is a measure of the change in strain with time when a constant stress is applied to the specimen. The tensile creep compliance $D(t)$ is given by:

$$D(t) = \frac{\varepsilon(t)}{\sigma_0}$$

(2.75)

where $\varepsilon(t)$ is the strain as a function of time and $\sigma_0$ is the constant tensile stress. The polymer response can be shown schematically by plotting log $D(t)$ against log time ($t$) (figure 2.4). After a short time the polymer chains have not begun to stretch and $D(t) = D_u$, the unrelaxed or glassy state. As $t$ nears the average relaxation time ($\tau_R$) a transition occurs to a more relaxed state. Following the transition a rubbery region is reached where $D(t) = D_R$, the relaxed compliance.
**FIGURE 2.4**

Typical creep compliance curves for linear and crosslinked polymers

![Creep Compliance Curves](image)

**FIGURE 2.5**

Typical relaxation modulus curves for linear and crosslinked polymers

![Relaxation Modulus Curves](image)
linked polymer $D(t)$ remains constant with a further increase in $t$. Linear polymers exhibit a second relaxation corresponding to the unravelling of chain entanglements and the onset of Newtonian flow.

Following a creep experiment the amount of 'set' can be determined by removing the applied stress and measuring the increase in original dimensions after a suitable time period. Periods of up to twenty four hours are employed to allow for delayed elastic recovery.

In a stress relaxation experiment stress decay with time is measured when a sample is subjected to an instantaneous strain. The tensile stress relaxation modulus $E(t)$ is given by:

$$E(t) = \frac{\sigma(t)}{\varepsilon_o}$$  \hspace{1cm} (2.76)

where $\sigma(t)$ is the stress as a function of time and $\varepsilon_o$ the constant tensile strain. At short times the glassy state has an unrelaxed modulus $E_u$ (figure 2.5). A transition state is encountered near $\zeta_R$ which is followed by the plateau region where a relaxed (rubbery) state is reached with modulus $E_R$. For a crosslinked polymer $E(t)$ remains constant, while the modulus for a linear polymer gradually decreases with the onset of flow, as a further function of time.

In dynamic mechanical experiments, a sinusoidal stress (or strain) is applied to a specimen and the resulting strain (or stress) is followed as a function of time (figure 2.6).

For an oscillating shear stress ($\sigma^s$) of frequency $\omega$ then

$$\sigma^s = \sigma_p^s \sin \omega t$$  \hspace{1cm} (2.77)

where $\sigma_p^s$ is the shear stress amplitude.
FIGURE 2.6
Oscillating stress or strain as a function of time

STRESS or STRAIN

\[ \sigma_f \]
\[ \varepsilon_f \]
\[ \delta \]
\[ \omega \]

TIME

\[ \frac{2\pi}{\omega} \]
Shear strain ($\varepsilon^S$) oscillates at the same frequency but lags by the phase angle $\delta$ such that:

$$\varepsilon^S = \varepsilon_p^S \sin(\omega t - \delta)$$

(2.78)

where $\varepsilon_p^S$ is the shear strain amplitude. A complex shear compliance $J^*(\omega)$ and complex shear modulus $G^*(\omega)$ can be defined, which have in phase $J'(\omega)$ and $G'(\omega)$ and out of phase $J''(\omega)$ and $G''(\omega)$ components.

$$|J^*(\omega)| = J'(\omega) \sin \omega t + J''(\omega) \cos \omega t$$

(2.79)

$$|G^*(\omega)| = G'(\omega) \sin \omega t + G''(\omega) \cos \omega t$$

(2.80)

$J'$ and $G'$ are the storage compliance and moduli and represent the energy stored by the sample. $J''$ and $G''$ are the loss compliance and moduli and represent input energy which has been dissipated as heat. The relationship between $J'$, $J''$ and $G'$ and $G''$ with $\log \omega$ is given in figures 2.7 and 2.8. At high $\omega$ glassy behaviour is exhibited, $J' = J_u$ and $G' = G_u$. At frequencies near $1/\tau_R$, $J'$ increases and $G'$ decreases rapidly as frequency decreases. $J''$ and $G''$ attain a maximum value at $1/\tau_R$. With a further decrease in frequency $J' = J_R$ and $G' = G_R$ and the polymer enters the rubbery state. At the onset of flow the linear polymer goes through a second relaxation with $J'$, $J''$ and $G''$ increasing and $G'$ decreasing with decreasing frequency. The relationship between loss and storage components for the complex compliance and modulus can be represented as shown in figure 2.9. It can be seen that

$$\tan \delta = \frac{J''}{J'} = \frac{G''}{G'}$$

(2.81)

where $\tan \delta$ is defined as the loss tangent.
FIGURE 2.7
Typical storage and loss compliance curves for linear and crosslinked polymers

FIGURE 2.8
Typical storage and loss modulus curves for linear and crosslinked polymers
Relationship between the loss and storage components for the complex modulus \((G^\ast)\) and complex compliance \((J^\ast)\)

**Figure 2.9**

Modulus-temperature curves for different polymer types

**Figure 2.10**
G* and J* can be represented by:

\[ G^* = G' + iG'' \quad (2.82) \]

and \[ J^* = J' - iJ'' \quad (2.83) \]

G', J' and G''J'' then become the real and imaginary components respectively.

If G' and J' are plotted against log (1/\(\omega\)) the curves correspond to G(t) and J(t) plotted against log t, where G(t) and J(t) are the shear equivalents of E(t) and D(t). The reciprocal relationship between frequency and time is a characteristic feature of linear viscoelasticity, with

\[ \tau = \frac{1}{\omega_{\text{max}}} \quad (2.84) \]

The above treatment assumes constant temperature, however relaxation times are dependent on temperature according to the equation:

\[ \tau = \tau_0 e^{\Delta H/RT} \quad (2.85) \]

where \(\Delta H\) is the enthalpy of the process and \(\tau_0\) is the relaxation time at a constant reference temperature \(T_0\).

The dependence of frequency can therefore be shown to be dependent on temperature according the equation for \(\omega_{\text{max}}\):

\[ \log (\omega_{\text{max}}) = \log \left(\frac{1}{\tau_0}\right) + \left(\frac{R}{\Delta H}\right)T \quad (2.86) \]

By holding \(\omega\) constant and varying T we can obtain plots of G', G'' and J', J'' versus temperature analogous to those for log \(\omega\). Increasing the
temperature increases molecular and segmental motions bringing a system more quickly to equilibrium or apparent equilibrium as a result of the acceleration of the various viscoelastic processes. A change in temperature is equivalent to shift along the time/frequency axis for a particular viscoelastic response. The shift factor \( a_T \) as defined by Williams, Landel and Ferry (159) is given by the equation

\[
\log a_T = \frac{c_1 (T-T_0)}{c_2 + (T-T_0)}
\]

(2.87)

c_1 and c_2 are constants which vary slightly from polymer to polymer. \( T_0 \) the reference temperature is often taken as the glass transition temperature (\( T_g \)) for the system.

2.6.3 Dynamic mechanical thermal analysis

Dynamic mechanical thermal analysis (DMTA) can be used to obtain modulus/temperature data useful for the evaluation of the mechanical characteristics of a polymer.

Figure 2.10 shows the curves for three types of homopolymers. Curve A, which represents a linear amorphous polymer, shows a dramatic modulus drop as the temperature is raised beyond that of its \( T_g \). If this polymer is crosslinked (curve B) a limiting modulus value would be obtained at its \( T_g \) and which would not change much with increase in temperature. This is a typical curve for a vulcanised conventional rubber. A crystalline polymer (curve C) shows two transition regions, the low temperature one representing \( T_g \) is followed by a gradual modulus drop until the second transition is reached, which corresponds to the melting point \( (T_m) \) of the crystalline structure. It is therefore apparent that modulus/temperature data can be used to identify different phases and their influence on modulus.
Extending this treatment to block copolymers, Bonart et al. (160) have suggested four types of curve are possible as shown in figure 2.11. Curve I represents an amorphous block copolymer of compatible components A and B exhibiting a single transition close to that for a random copolymer of A and B, and as a result no phase separation occurs. If partial microphase separation occurs and a certain amount of random block units exist between the phases, a curve with a gradual modulus drop with temperature may be obtained (curve II) or one where modulus remains constant over a particular temperature range (curve III), the exact shape being dependent on morphology. When phase separation is complete (curve IV) a long modulus plateau region is obtained between the glass transition temperatures of the respective components. In comparison to the random copolymer type curve I the two phase system is not affected significantly by compositional variations, i.e. the actual plateau temperature range \( T_g(A) \) to \( T_g(B) \) does not change with composition. The composition can however affect the position of the plateau modulus as shown for curve IV.

2.6.4 Glass Transitions in Copolymers

Random copolymers exhibit a \( T_g \) somewhere intermediate between those of the respective homopolymers, the actual value of \( T_g \) depending on the relative amounts of each component present. According to the Gordon-Taylor equation (161) for a random copolymer made up of monomers A and B:

\[
T_g = \frac{T_g(A) - w_B \left[ \frac{K T_g(B) - T_g(A)}{1 + w_B (K - 1)} \right]}{1 + w_B (K - 1)} \tag{2.88}
\]

where \( w_B \) is the weight fraction of component B and \( T_g(A) \), \( T_g(B) \) the glass transition temperatures of the homopolymers A and B. \( K \) is a constant expressed in terms of the thermal expansion coefficients of the homopolymers in the glassy and rubber state. A similar expression for the \( T_g \) of a random copolymer has been given by Wood (162):
FIGURE 2.11  
Dependence of modulus-temperature curves on block copolymer morphology (160)
where $T_g$ values are given in Kelvin units.

For a block copolymer the number of glass transition temperatures will be determined by the phases present and hence by the block lengths and the interaction between monomer units (see section 2.7). Copolymers of the AB and ABA type where the blocks are long, phase separate and two $T_g$ values close to their homopolymers are observed. Differences in the $T_g$ values between those of the block copolymer and the homopolymers can be related to block length.

The effect of block molecular weight on $T_g$ can be shown by the Flory-Fox equation (163):

$$\frac{1}{T_g} = \frac{\omega_A}{T_{g(A)}} + \frac{\omega_B}{T_{g(B)}}$$  \hspace{1cm} (2.89)

where $T_g$ values are given in Kelvin units.

The effect of block molecular weight on $T_g$ can be shown by the Flory-Fox equation (163):

$$T_g = T_{g\infty} - \frac{K}{\bar{M}_n}$$  \hspace{1cm} (2.90)

where $T_{g\infty}$ is the glass transition at infinite molecular weight and $K$ is a positive constant.

If phase separation is incomplete a region exists between the phases which is composed of random blocks and which has a $T_g$ somewhere between $T_g(A)$ and $T_g(B)$. Knowing the amounts of each component present in the mixed phase, equation (2.89) can then be used to determine the intermediate $T_g$.

2.6.5 Models for Two Phase Systems

The modulus of a crosslinked elastomer will be increased by the presence of a solid filler. One of the earliest attempts to quantify this was by Smallwood (164) who used an expression derived from Einstein's viscosity equation (165),

$$E = E_0 (1 + 2.5\phi)$$  \hspace{1cm} (2.91)
where $E$ is the modulus of the filled rubber, $E_0$ the modulus of the unfilled rubber matrix and $\phi$ the volume fraction of filler. This equation holds only for low filler concentrations. At higher concentrations consideration must be given to the interactions between pairs of particles, Guth and Gold (166) introduced a squared term into the above equation to account for this:

$$E = E_0 \left(1 + 2.5\phi + 14.1\phi^2\right)$$

(2.92)

For non-spherical particles Guth (167) introduced a shape factor ($F$)

$$E = E_0 \left(1 + 0.67F\phi + 1.62F^2\phi^2\right)$$

(2.93)

where $F$ is expressed as the ratio of the diameter to width of particles. In the case of heterogeneous block copolymer systems where a glassy phase is dispersed in a rubbery matrix the glassy domains can be regarded as filler particles. Considering these block copolymers as 'microcomposite' materials enables 'mechanically equivalent models' to be used to describe their tensile behaviour. In principle, these assign various amounts of parallel and series coupling to the two phase structure. The Takayanagi (168) model for a homogeneously mixed two phase system, together with its schematic representation, is given in figure 2.12. The two parameters $\phi$ and $\lambda$ represent the state of mixing of the two phases, but only one is independent. The product $\phi\lambda = v_2$, the volume fraction of the dispersed phase. The solution for the Takayanagi model is

$$E^* = \left[\frac{E_2^* + \phi}{E_2^* + (1-\lambda)E_1^*}\right] + \left[\frac{1 - \phi}{E_1^*}\right]$$

(2.94)
FIGURE 2.12
The Takayanagi model
where \( E^* \) is the complex modulus for the system and \( E_1^* \) and \( E_2^* \) are the complex moduli of the components. When the particles are spherical the coupling constants \( \lambda \) and \( \beta \) can be expressed in the form of volume fractions

\[
\lambda = \frac{(3v_2 + 2)}{5} \quad (2.95)
\]

\[
\beta = \frac{5v_2}{(2 + 3v_2)} \quad (2.96)
\]

Other models describing two phase behaviour have been proposed (197-200) however to obtain values for the 'composite modulus' lengthy calculations are often required.

2.6.6 Ultimate Properties

Failure of elastomers at high extension is a poorly understood phenomenon. It is considered that in a randomly formed network certain chains are under much higher stress than others (169). Indeed it is largely this factor which causes deviation from ideal stress-strain behaviour. Once one network strand fails others take more stress and will generally fail by a 'domino' effect.

In filled rubbers and elastomeric two phase block copolymers the stress in regions of incipient failure is spread over a large numbers of network chains by the 'filler' particles (170). This is analogous to the 'blunting' of cracks in plastic failure (171). There is no adequate theory describing this effect for rubbers at high elongation.

Considering thermoplastic elastomers in more detail, the stress-strain curves and ultimate properties have been shown empirically to be dependent on several factors such as structure, composition, block molecular weight and polydispersity. Several authors (172-174) have reviewed these
effects for a wide range of copolymers. Tensile strength and elongation at break values are given in table 2.2 for several copolymers with varying structure, composition and polymer type. There are large differences between star, graft and linear block copolymers of similar polystyrene/polybutadiene composition. Likewise, differences can be observed for fixed composition ABA copolymers of different block types. Increasing the styrene content in styrene-butadiene-styrene from 13 to 28% wt. increases the tensile strength considerably. However further increases in styrene content reduce elongation. The stress-strain curves for a range of styrene-butadiene-styrene compositions, with an overall constant molecular weight, are given in figure 2.13 (4).

The dependence of tensile strength and elongation at break on temperature and extension rate often leads to difficulties in interpreting different sets of data. However, comparisons can be made when using the failure envelope (201, 202). A typical plot is given in figure 2.14. The envelope is independent of temperature, time to break and strain rate. Area A to the left of the curve indicates stable levels of stress and strain. Values in region B will cause rupture. The arrow indicates direction of lower temperatures or higher strain rates.
TABLE 2.2
Tensile Properties of Several Linear and Branched Block Copolymers

<table>
<thead>
<tr>
<th>Copolymer type(^{a})</th>
<th>Block A</th>
<th>Block B</th>
<th>A content (% wt.)</th>
<th>Tensile strength, (\sigma_b) (MPa)</th>
<th>Elongation at break, (\varepsilon_b) (%)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>((AB)_6)(^{b})</td>
<td>Polystyrene</td>
<td>Polybutadiene</td>
<td>30</td>
<td>42.0</td>
<td>730</td>
<td>89</td>
</tr>
<tr>
<td>BgA (^{c})</td>
<td>Polystyrene</td>
<td>Polybutadiene</td>
<td>34</td>
<td>11.0</td>
<td>900</td>
<td>18</td>
</tr>
<tr>
<td>ABA</td>
<td>Polystyrene</td>
<td>Polybutadiene</td>
<td>13</td>
<td>1.0</td>
<td>1000</td>
<td>4</td>
</tr>
<tr>
<td>ABA</td>
<td>Polystyrene</td>
<td>Polybutadiene</td>
<td>28</td>
<td>23.1</td>
<td>1030</td>
<td>4</td>
</tr>
<tr>
<td>ABA</td>
<td>Polystyrene</td>
<td>Polyisoprene</td>
<td>33</td>
<td>26.0</td>
<td>1000</td>
<td>21</td>
</tr>
<tr>
<td>ABA</td>
<td>Poly((\alpha)-methyl styrene)</td>
<td>Polyisoprene</td>
<td>33</td>
<td>45.5</td>
<td>900</td>
<td>21</td>
</tr>
<tr>
<td>ABA</td>
<td>Poly((\alpha)-methyl styrene)</td>
<td>Poly(propylene sulphide)</td>
<td>30</td>
<td>18.0</td>
<td>900</td>
<td>175</td>
</tr>
</tbody>
</table>

\(^{a}\) For nomenclature see Appendix

\(^{b}\) Linking agent (\(X\)) is divinylbenzene

\(^{c}\) Average of 10 graft sites for chain
FIGURE 2.13
Dependence of stress-strain properties on weight percent of styrene units for styrene-butadiene-styrene (4)

FIGURE 2.14
Typical failure envelope for a rubber vulcanisate
2.7 PHASE SEPARATION IN AMORPHOUS BLOCK COPOLYMERS

The thermodynamic criteria for the mixing of two or more systems is that the Gibbs free energy ($\Delta G$) is negative

$$\Delta G = \Delta H - T\Delta S$$  \hspace{1cm} (2.97)

where $\Delta H$ and $\Delta S$ are the enthalpy and entropy of mixing respectively and $T$ is the absolute temperature. The enthalpy of mixing for a pair of homopolymers can be given by the Van Laar-Scatchard-Hildebrand equation

$$\Delta H = \frac{KTV}{V_r} v_A v_B \chi_{AB} (1 - 2/z)$$  \hspace{1cm} (2.98)

where $V$ is the total volume of the system, $T$ is the absolute temperature, $K$ is the Boltzmann constant, $V_r$ is the volume of a lattice site, $z$ is the coordination number of the lattice, $v_A$ and $v_B$ are the volume fractions of polymers A and B and $\chi_{AB}$ is the interaction parameter between A and B.

Applying the lattice treatment to obtain an expression for the entropy of mixing of two homopolymers

$$\frac{\Delta S}{R} = -N_A \ln v_A - N_B \ln v_B$$  \hspace{1cm} (2.99)

where $R$ is the gas constant, $N_A$ and $N_B$ are the number of moles of homopolymers A and B. The entropy gained from the mixing of polymers is usually small, and therefore miscibility will be determined by the sign and magnitude of $\Delta H$. Scott (176) derived an expression for the interaction parameter ($\chi_{AB}^{CR}$) at the critical point of phase separation ($\Delta G = 0$) in terms of the degree of polymerisation of each homopolymer. Values of ($\chi_{AB}^{CR}$) approached zero as molecular weight increased. For the case of a mixture of two polymers of infinite molecular weight a small
positive $\Delta H$ value will be sufficient to overcome the entropy of mixing and phase separation will occur. For two dissimilar polymers mixing does not usually occur. The thermodynamic treatment of phase separation in block copolymers has been studied by several workers (177-182, 184, 195, 196).

Krause (177) derived an expression for $\chi_{AB}^{cr}$ for block copolymers from the enthalpy and entropy of mixing for homopolymers. She assumed the polymers were monodisperse with sharp boundaries between phases and that there was no loss of molecular disorder within phases. In later papers (178, 179) Krause modified the entropy expression to include terms accounting for the loss in entropy at the interphase due to the immobilisation of the block linking segments. The entropy change per copolymer molecule when microphase separation occurs is given by

$$\frac{\Delta S}{K} = (v_A \ln v_A + v_B \ln v_B) - 2(m-1)\langle\frac{\Delta S_d}{R}\rangle + \ln(m-1)$$

(2.100)

where $m$ is the number of blocks in the copolymer molecule and $\Delta S_d/R$ is the disorientation entropy gain on fusion per segment of a polymer. The first term on the right hand side of the equation is concerned with the decrease in available volume for each block in the molecule after microphase separation, assuming there is no volume change on mixing. The second term is the additional entropy decrease caused by immobilisation at the interphase surface of the units which link the blocks in each copolymer molecule. If the number of blocks in the copolymer is large ($m \gg 3$) a third term is included which accounts for the large number of sites available for the block linking segments on the surface between microphases.

Possible values of $\Delta S_d/R$ cover a wide range depending on the chemical nature of the blocks, as a result Krause was unable to predict whether block copolymers underwent phase separation more easily than
their corresponding homopolymer mixtures. However the treatment is useful in that no matter what values are used for $\Delta S_d/k$ the entropy change on microphase separation determined from equation (2.100) becomes more and more negative as the number of blocks in each copolymer molecule increases. In other words, entropy considerations will make phase separation more difficult as the number of blocks per molecule increases. Similarly for molecules having the same chain length and the same number of blocks a copolymer with very different $v_A$ and $v_B$ (e.g. 0.25 and 0.75 respectively) will undergo phase separation less readily than one with $v_A = v_B$. Krause has also considered the case in which homopolymer of one component is present as an impurity in the copolymer system (179).

The morphology of block copolymers differs from that found in homopolymer phase separated mixtures. The chemical bonding between the blocks limits the size to which the phases can grow. Phase separation in block copolymers can often be regarded as a continuous uniform matrix of one block type with the other block dispersed as discrete domains within it. These domains, being a lot smaller than the aggregates associated with homopolymer mixtures, are usually not capable of scattering visible light and as a result the copolymer appears transparent. It is due to the limited domain size that the morphology in block copolymers is referred to as microphase separation.

An expression was derived by Meier (180, 181) relating the domain dimensions with the length of the A block in an AB copolymer. He was also able to predict from $(X_{AB})_{cr}$ values obtained at $\Delta G = 0$, in a similar manner to Krause, that microphase separation occurs at higher degrees of polymerisation per block than for the corresponding homopolymers. Therefore, two homopolymers are less miscible as separate molecules than they are when linked into a block copolymer molecule.
Bianchi and coworkers (182) put forward a statistical thermodynamic expression for microphase separation in ABA block copolymers. The average equilibrium domain size was determined from interfacial surface free energy values. The theory also predicted that domain size decreased with increasing temperature. This is important when comparing the experimental and predicted values for domain size for systems where the glassy domains have glass transition temperatures \( T_g \) above the temperature at which they are being measured.

Three morphological types have been suggested for AB and ABA block copolymers - spheres, rods (or cylinders) and lamellae. The effect of block copolymer composition on these forms for solvent cast samples has been summarised by Molau (183),

\[
\begin{array}{cccccc}
\text{Increasing A content} & \text{Increasing B content} \\
\text{A spheres in B matrix} & \text{A matrix} & \text{B spheres in A matrix} \\
\text{A rods in alternative B rods in} & \text{B matrix} & \text{lamellae} & \text{A matrix} & \text{A matrix} \\
\end{array}
\]

the morphology being determined by micelle formation at a critical solution concentration (approx. 10% w/v), and it is assumed that this persists through the drying process until the solid state is reached.

Meier (180) determined for an AB block copolymer the relative free energies for each domain structure and related these with the molecular weight ratios of the two blocks. Since the fine structure that has the lowest free energy will be the one to appear, these results (figure 2.15) predict spheres at molecular weight ratios, \( M_B/M_A \), from infinity to four, a short range of compositions giving rise to cylinders and the existence of alternating lamellae at midrange compositions.

Inoue (184) using a dilute solution thermodynamic approach also predicted for AB block copolymers the occurrence of spheres, rods and lamellae but over slightly different compositional ranges from those obtained by Meier.
Relative free energy for each morphological form as a function of block molecular weight ratio (180)
The morphology of commercial styrene-butadiene-styrene thermoplastic elastomers with a styrene content of 25 to 30% vol. has been determined by electron microscopy (185-187) and found to consist of, in its simplest form, regularly spaced spheres of styrene dispersed in a continuous matrix of polybutadiene. Small angle x-ray scattering (SAXS) data (188-190) has confirmed this microlattice arrangement which can be likened to the three-dimensional array of atoms in a crystal lattice. Applying the Bragg equation, interdomain distances of 300 to 500 Å have been obtained. The diameter of the polystyrene spheres obtained from SAXS were between 100 and 400 Å.

In addition to composition affecting morphology, sample history is also an important factor. The use of different casting solvents (190-192) and the rate at which it is removed (193) are known to have a considerable influence on the resulting morphology. Sample extrusion has also been shown (194) to influence morphology.

The original concept of sharp boundaries between phases was modified by Marker (195) to include a diffuse region between the phases consisting of a mixture of A and B components. Leary and Williams (196) calculated values for the interfacial thickness (ΔR) for a styrene-butadiene-styrene block copolymer. For spherical domains of 200 Å in diameter, free energy values suggested unstable structures for ΔR = 20 or 60 Å but a stable structure for ΔR = 40 Å.
CHAPTER 3

EXPERIMENTAL

SECTION A: POLYMER SYNTHESIS

3.1 PURIFICATION OF REAGENTS

3.1.1 High vacuum techniques

Methods similar to those described by Petters (19, 36) were employed. The high vacuum apparatus, made from pyrex glass tubing, consisted of a wide bore primary manifold connected to two smaller bore secondary manifolds (figure 3.1). Each of these secondary manifolds was equipped with greaseless p.t.f.e. 'O' ring joints (203) to which flasks and reaction vessels could be attached. The joints and manifolds could be isolated from each other by suitably placed greaseless p.t.f.e. 'O' ring taps (203). A mercury diffusion pump and a rotary oil pump connected in series were used to produce the vacuum in the system. The pressure in the vacuum line was measured using a Pirani gauge. Pressures below 0.1 Pa were obtained. Two cold taps (liquid nitrogen) were used to condense out any gas or gases present in the apparatus and also to prevent the passage of mercury vapour into the manifolds and rotary pump. Taps situated at either end of the primary manifold were used to isolate the pumps and Pirani gauge during argon blanket procedures. To fill the reaction vessels and collection flasks with argon it was necessary to flood the primary and secondary manifolds with the inert gas. The gas was bled into the system through one of the secondary manifold joints and the pressure monitored by means of a mercury loot attached to the main manifold. The loot also served as a relief valve if overpressurisation of the system occurred.

Prior to use on the vacuum line all glassware was thoroughly cleaned with chromic acid, washed with distilled water, rinsed with acetone and
then dried at 110°C for several hours. Glassware, after being attached to the vacuum line and evacuated, was strongly flamed to remove any adsorbed moisture still remaining.

Cyclohexane (Fisons, SLR grade, 99.5% pure) was stored over molecular sieves for several weeks before being dried on the vacuum line. Flasks containing the solvent and finely ground calcium hydride were attached to the vacuum line via the p.t.f.e. joints. Evacuation was achieved by first freezing the solvent using liquid nitrogen and then opening the taps on the manifold arm to the vacuum system. When the reading on the gauge had returned to a stable low value the taps were closed and the solvent then thawed. The solvent was then continuously stirred for several days using a magnetic follower. During this period freeze, degas, thaw cycles were carried out, as described by Fetters (19), until no further gas evolution could be detected by the pressure gauge. The solvent was then distilled over a succession of freshly prepared sodium mirrors until no visible degradation of the mirror occurred at room temperature. One or two mirrors were usually all that were required if the solvent had been thoroughly dried over calcium hydride first.

n-Heptane (BDH, 99.5% pure) was treated in an identical manner to the cyclohexane.

Tetrahydrofuran (THF) (BDH, 99.5% pure, containing 0.1% w/v hydroquinone as stabiliser) stored over calcium hydride was distilled onto freshly ground calcium hydride on the vacuum line. Stirring and degassing were carried out as above until no further gas evolution was detectable. The solvent was then distilled into a flask containing a small quantity of sodium metal and several cm³ of dried α-methylstyrene monomer. In the absence of any reactive impurities a deep red colour formed in the solution, indicating the formation of the 'living' disodium α-methylstyrene tetramer. If no colouration occurred, the THF was distilled onto a
further quantity of calcium hydride and the whole procedure repeated. The distillation process was found to be sufficient to destabilise the solvent. Prolonged storage of THF in a destabilised form was avoided because of the possibility of the formation of highly reactive peroxides. As an added precaution against peroxide formation, flasks containing THF were always covered with aluminium foil to shield them from direct sunlight.

Styrene (Fisons, Pure Grade, containing 10-15 ppm t-butyl catechol as stabiliser) stored over calcium hydride was distilled onto freshly ground calcium hydride on the vacuum line. The resulting slurry was stirred and periodically degassed over several days. During this period the viscosity of the styrene increased due to the formation of small amounts of low molecular weight polystyrene. The monomer was then flash distilled onto a succession of sodium mirrors prior to use. Styrene cannot be exposed to a sodium mirror for more than several hours because polymerisation by sodium initiation occurs. When storage of styrene in a dry state was required it was distilled from the sodium mirrors into a flask containing n-butyl,s-butyl magnesium (Lithium Corp. of America). After several hours at room temperature the styrene turned bright yellow as the result of initiation by the magnesium compound. The propagation rate of this reaction is so slow at room temperature that the styrene could be left for several days without any appreciable polymer forming.

α-Methylstyrene (Koch Light, Pure Grade, containing 10-15 ppm 2,4-dimethyl-6-t-butylphenol as stabiliser) was purified in a similar way to styrene. Prolonged storage of the monomer over sodium mirrors was possible because α-methylstyrene has a very low ceiling temperature (204) and at room temperature negligible amounts of polymer will form.

The relatively few stages needed in the purification of the styrene and α-methylstyrene suggested the distillation process was sufficient
for the removal of stabiliser.

Vinyltoluene (Fluka A.G., Pure Grade, mixture of meta and para isomers) was purified in a similar way to styrene.

Isoprene (Aldrich, Gold Label) was purified over calcium hydride and sodium mirrors as for styrene and then stored at 0°C until required.

N,N,N',N' Tetramethylethylenediamine (TMEDA) (Fluka A.G., 99% pure) was stored on the vacuum line over finely ground calcium hydride. Only a few freeze, degas, thaw cycles were required before no further gas evolution was detectable.

s-Butyl lithium (s-BuLi) (Aldrich) was supplied as a solution in cyclohexane (approx. 1.2 M). No purification was necessary and it was stored under argon at a slight positive pressure in bottles equipped with self-sealing rubber septa. Standardisation of the solution was carried out prior to each preparation using the Gilman-Haubein double titration method (205). A 1 cm³ aliquot of s-BuLi, extracted from the storage bottle by syringe, was hydrolysed in 10 cm³ of distilled water. The resulting alkalinity of the solution was determined by titration with 0.1 M hydrochloric acid solution using phenolphthalein as the indicator. A second 1 cm³ aliquot of S-BuLi was added to 10 cm³ dry diethyl ether containing 1 cm³ of benzyl chloride. After agitating the solution for one minute 10 cm³ of distilled water was added. The two layer mixture was stirred and its alkalinity determined as above. The first titration determines the total alkalinity of the initiator solution whereas the second titration determines the residual alkalinity due to any material originally present which does not contain carbon-lithium bonds, e.g. lithium hydroxide. The difference between the titration values gives the amount of material which has reacted with the benzyl chloride and therefore a reasonably accurate measure of the amount of active s-BuLi present.
3.1.2 Purification under Dry Nitrogen

Oxygen-free nitrogen (BOC 'White Spot') was dried by passing through successive columns of molecular sieves, silica gel and calcium hydride and then through a bubbler containing concentrated sulphuric acid. To prevent the passage of acid vapour into the purification apparatus the nitrogen was passed through a trap cooled with solid carbon dioxide.

n-Heptane (BDH, 99.5% pure) which had been stored over molecular sieves for several weeks was transferred to a flask containing finely ground calcium hydride and fitted with a nitrogen inlet and condenser (figure 3.2). Dry nitrogen was bubbled through the solvent for several hours. During this period the mixture was continuously stirred by magnetic follower. The heptane was then distilled direct into a reaction vessel connected to the condenser. Using a very narrow boiling range over which the solvent was collected the initial and final fractions were removed using a pig fitting.

Cyclohexane (Fisons, SLR Grade, 99.5% pure) was dried and distilled in a similar manner to heptane.

Isoprene (Aldrich, Gold Label) was degassed and dried as above and then distilled into a collection flask fitted with a rubber septum (figure 3.2). The isoprene could then be transferred to the reaction flask using a hypodermic syringe.
nitrogen supply

tap to control flow

thermometer

oil bath
calcium hydride
heater/stirrer

rubber septum

Solvent Distillation Apparatus

Isoprene Distillation Apparatus

calcium chloride

trap to prevent air entry

water bath
3.2 INITIAL STUDY OF ANIONIC GRAFTING TECHNIQUES

To achieve conditions of rigorous purity necessary for the synthesis of polymers by anionic methods, two gas blanket methods were investigated. In the first method the reagents were dried under vacuum and/or dry nitrogen and the polymerisations carried out under nitrogen blanket. In the second method all reagents were dried under vacuum and the polymerisations carried out under argon.

3.2.1. Nitrogen blanket methods

This method was used for the preparation of polyisoprene and polyisoprene-\(g\)-polystyrene using either n-heptane or cyclohexane as the solvent. (See Appendix for explanation of nomenclature.)

Polyisoprene and polyisoprene-\(g\)-polystyrene

The solvent, dried and distilled under nitrogen, was collected in a graduated reaction vessel fitted with nitrogen bubbler, gas outlet and rubber septum (see figure 3.2). Stirring and purging of solvent with nitrogen was then carried out for several hours. The bubbler was then raised above the level of the solvent and the nitrogen flow rate reduced until it was just detectable. Isoprene, previously distilled under nitrogen into a flask fitted with rubber septum, was transferred to the reactor using a syringe which had been thoroughly flushed several times with dry nitrogen. A calculated volume of initiator, s-ButLi, was syringed into the reactor direct from the storage bottle. The solution was then stirred for 3 to 23 hours at 20 or 50°C. At the end of this polymerisation period the living polyisoprenyllithium solution was terminated by the addition of a small quantity of 2-propanol (Fisons, SLR grade). Only an amount sufficient to 'kill off' the polymer was used (< 0.2 cm\(^3\)). A sample (5 cm\(^3\)) was then extracted by syringe and precipitated in an excess
(x 4) quantity of alcohol (methanol or 2-propanol). For the polyisoprene only preparation (sample H1) the total quantity of product was precipitated at this point. The polyisoprene was dried to constant weight in a vacuum oven at elevated temperature. The samples were analysed by g.p.c.

Site initiation (metalation) of the polyisoprene remaining in the reactor was achieved by adding a calculated amount of metalating agent, s-BuLi.TMEDA. The transfer of TMEDA from the vacuum line to the reactor was carried out as follows; from the storage flask the TMEDA was distilled into a collection flask fitted with a rubber septum (figure 3.3). A connection from the argon cylinder or dry nitrogen supply was then attached to the vacuum line, the manifolds were isolated as mentioned in section 3.1.1 and the vacuum line pressurised until the mercury column had dropped to a level slightly below the surface of the mercury reservoir. The tap to the TMEDA flask was carefully opened and a slight positive pressure maintained. TMEDA could then be removed from the collection flask by syringe and transferred to the reactor. The s-BuLi was transferred by syringe direct to reactor from the storage bottle as before. The reaction was allowed to proceed for 1 to 3 hours at 20 or 50°C, during this period the viscosity of the solution noticeably increased. At the end of the metalation period a second sample was removed, precipitated and dried as before and then analysed by g.p.c. A calculated quantity of styrene was then added to the reactor, the transfer method being the same as that used for TMEDA. The addition of the styrene turned the solution a bright red colour indicating the initiation of the monomer and the formation of polystyryllithium. Polymerisation was carried out for a period of 7 to 20 hours at the temperature used for metalation. The initial addition of the styrene caused a noticeable drop in solution viscosity, however, after several minutes the viscosity started to increase again. These changes can be
FIGURE 3.3
Flasks used for high vacuum drying and transfer procedures.

FIGURE 3.4
THF transfer apparatus.
attributed to living end associations (see sections 2.1.1 and 2.1.2). The reaction was terminated by the addition of sufficient 2-propanol to just turn the solution colourless. This was accompanied by a viscosity drop, which indicated that the chain end associations had been destroyed. Polymer precipitation was carried out as before with the product being dried to constant weight in a vacuum oven. A small amount (\(< 0.1\) g) of product was used for g.p.c. analysis.

A summary of the experimental conditions used for the preparation of several samples is given in table 3.1.

One of the major problems associated with anionic polymerisations is premature termination due to the presence of reactive impurities and because polyisoprenyllithium does not have a well defined colour in hydrocarbon solvent it is difficult to ascertain whether polymerisation has occurred and if so for how long. To circumvent these difficulties several modifications to the above polymerisation/metalation procedures were included:

Samples G3, G4 - as a check to ensure that initiation would occur a trace amount of s-BuLi (\(< 1\%\) of total initiator used) and a few drops of styrene (approx. 0.1 g) were added to the solvent prior to the addition of monomer. The resulting red solution colourations indicated that the solvents were not excessively contaminated.

Samples G2, G3, G4 - to check that polyisoprenyllithium was still present at the end of the polymerisation period a few drops of styrene (approx. 0.1 g) were added to the solution. The solutions turned a red colour when a small quantity of TMEDA (\(< 1\%\) of total used) was added, confirming the presence of a living system.

Samples G1, G2 - a further method of ensuring complete polymerisation of isoprene was to add a second quantity of initiator (\(< 1\%\) of total) at the end of the allocated isoprene polymerisation period and the solution
### TABLE 3.1
Experimental Conditions for the Preparation of Polyisoprene and Polyisoprene-g-polystyrene

<table>
<thead>
<tr>
<th>Sample ref.</th>
<th>Blanket method</th>
<th>Solvent</th>
<th>Isoprene conc. (% w/v)</th>
<th>s-BuLi (moles/10^-5 g isoprene)</th>
<th>time (hours)</th>
<th>s-BuLi (moles/10^-5 g isoprene)</th>
<th>Molar ratio [THFEDA]/[s-BuLi]</th>
<th>time (hours)</th>
<th>styrene (% wt. total monomer feed)</th>
<th>time (hours)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H1</td>
<td>Nitrogen</td>
<td>n-Heptane</td>
<td>11.4</td>
<td>6.4</td>
<td>20.0</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>G1^a</td>
<td>Nitrogen</td>
<td>n-Heptane</td>
<td>8.2</td>
<td>4.9</td>
<td>20.0</td>
<td>6.6</td>
<td>4.8</td>
<td>3.0</td>
<td>32.5</td>
<td>20.0</td>
</tr>
<tr>
<td>G2</td>
<td>Nitrogen</td>
<td>n-Heptane</td>
<td>10.9</td>
<td>4.2</td>
<td>6.0</td>
<td>5.3</td>
<td>3.8</td>
<td>2.0</td>
<td>35.8</td>
<td>13.0</td>
</tr>
<tr>
<td>G3</td>
<td>Nitrogen</td>
<td>n-Heptane</td>
<td>4.5</td>
<td>11.8</td>
<td>5.0</td>
<td>5.7</td>
<td>8.5</td>
<td>1.0</td>
<td>25.3</td>
<td>15.0</td>
</tr>
<tr>
<td>G4</td>
<td>Nitrogen</td>
<td>n-Heptane</td>
<td>6.4</td>
<td>8.0</td>
<td>3.5</td>
<td>6.3</td>
<td>5.6</td>
<td>1.3</td>
<td>22.0</td>
<td>16.0</td>
</tr>
<tr>
<td>G5^a</td>
<td>Nitrogen</td>
<td>Cyclohexane</td>
<td>2.8</td>
<td>9.2</td>
<td>23.0</td>
<td>14.1</td>
<td>5.6</td>
<td>2.0</td>
<td>39.3</td>
<td>14.0</td>
</tr>
<tr>
<td>G6</td>
<td>Nitrogen</td>
<td>n-Heptane</td>
<td>9.5</td>
<td>3.2</td>
<td>12.0</td>
<td>7.7</td>
<td>7.3</td>
<td>3.0</td>
<td>19.2</td>
<td>7.0</td>
</tr>
<tr>
<td>G7^a</td>
<td>Nitrogen</td>
<td>Cyclohexane</td>
<td>4.5</td>
<td>3.5</td>
<td>2.8</td>
<td>5.3</td>
<td>—</td>
<td>2.0</td>
<td>28.8</td>
<td>16.0</td>
</tr>
<tr>
<td>G8</td>
<td>Argon</td>
<td>n-Heptane</td>
<td>20.0</td>
<td>1.1</td>
<td>5.0</td>
<td>9.4</td>
<td>1.0</td>
<td>2.0</td>
<td>42.0</td>
<td>4.0</td>
</tr>
<tr>
<td>G9</td>
<td>Argon</td>
<td>Cyclohexane</td>
<td>6.0</td>
<td>2.0</td>
<td>6.0</td>
<td>10.0</td>
<td>1.0</td>
<td>1.0</td>
<td>21.9</td>
<td>3.0</td>
</tr>
</tbody>
</table>

*^a*) Preparations carried out at 50°C, all other preparations at 20°C.
then stirred for a further 4 hours before terminating. A sample was extracted for g.p.c. analysis prior to the second initiator addition. Sample G7 - to determine whether TMEDA was actually necessary for the grafting reaction to take place, no TMEDA was used.

3.2.2 Argon Blanket Method

All the reagents (except s-BuLi) were dried and distilled under vacuum. Argon (BOC, 99.98% pure) was used as obtained.

The method was used for the synthesis of two types of isoprene graft copolymers, namely polyisoprene-g-polystyrene and polyisoprene-g-poly(α-methylstyrene). An attempt was also made to graft a conventional rubber, EPDM, with styrene.

3.2.2.1 Polyisoprene-g-polystyrene

Solvent was distilled from a storage flask into a flamed out graduated reaction vessel (figure 3.3). Isoprene was then distilled into a graduated measuring vessel (figure 3.3) and a measured quantity distilled into the reactor containing the solvent. At this point styrene and TMEDA were distilled from their respective storage flasks into collection vessels fitted with rubber septa (figure 3.3). The reactor and collection flasks were then pressurised with argon as mentioned in section 3.2.1.1. The methods for the transfer of reagents and the polymerisation and metalation procedures were then followed as for the nitrogen blanket preparation of polyisoprene-g-polystyrene. The experimental conditions for the two samples prepared (G8 and G9) are given in table 3.1. The isoprene termination step was omitted from sample G9.

3.2.2.2 Polyisoprene-g-poly(α-methylstyrene)

Using cyclohexane as the solvent the isoprene polymerisation and metalation reactions were carried out in the same way as in the above
preparations. Unlike styrene, \(\alpha\)-methylstyrene has a low ceiling temperature and therefore to achieve appreciable conversion of the monomer to polymer, the polymerisation of \(\alpha\)-methylstyrene must be carried out at temperatures below 0°C (206). Cyclohexane freezes at 4°C and therefore to carry out polymerisations below this temperature the addition of a second solvent with a low freezing point is required. A polar solvent, THF, with a freezing point of \(-108^\circ\)C was used. The effect of polar solvents on diene microstructure (see section 2.1.4) and the possible interference with the metalation reaction suggested that the THF should be added after the \(\alpha\)-methylstyrene addition. The monomer was transferred to the reactor using the same method as for styrene. The initial transfer of THF to the reactor was carried out under vacuum, however, because this involved the freezing of the polymer solution and the re-evacuation of the reactor which were both very time consuming processes, a second method of THF transfer was considered. This involved the transfer of THF under argon pressure. The THF was first distilled under vacuum from the storage flask into a flask fitted with two rubber septa. Using the set-up shown in figure 3.4, a controlled amount of THF was then transferred into the reactor by creating a flow of argon in the system. The entry of air was prevented by maintaining a positive argon pressure throughout the transfer. The needles were then removed and the reactor placed in a low temperature insulated methanol bath. Temperatures in the range 0 to \(-45^\circ\)C were achieved using a cooling coil connected to a Statim refrigeration unit and temperatures in the range \(-45\) to \(-76^\circ\)C obtained using a Townson and Mercer thermostat heat exchange unit cooled with solid carbon dioxide.

The experimental conditions for the samples prepared are given in table 3.2. To ensure that isoprene polymerisation was complete prior to metalation a second quantity of initiator was added and the temperature
TABLE 3.2
Experimental Conditions for the Preparation of Polyisoprene-g-poly(α-methylstyrene)

<table>
<thead>
<tr>
<th>Sample ref.</th>
<th>Blanket Method</th>
<th>Solvent</th>
<th>Isoprene conc. (% w/v)</th>
<th>$s$-BuLi (moles/ $10^{-5}$ g isoprene)</th>
<th>Polymerisation</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>time (hours)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>temp. (°C)</td>
</tr>
<tr>
<td>S1</td>
<td>Argon</td>
<td>Cyclohexane</td>
<td>6.1</td>
<td>4.6</td>
<td>12</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1.5</td>
<td>0.2</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>20</td>
</tr>
<tr>
<td>S2</td>
<td>Argon</td>
<td>Cyclohexane</td>
<td>6.8</td>
<td>4.0</td>
<td>15</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.9</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>50</td>
</tr>
</tbody>
</table>

Metalation

<table>
<thead>
<tr>
<th>Sample ref.</th>
<th>$s$-BuLi (moles/ $10^{-5}$ g isoprene)</th>
<th>molar ratio $[TMEDA] /[s$-BuLi]</th>
<th>Metalation</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>time (hours)</td>
</tr>
<tr>
<td>S1</td>
<td>9.4</td>
<td>2.9</td>
<td>4.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>20</td>
</tr>
<tr>
<td>S2</td>
<td>9.6</td>
<td>3.4</td>
<td>2.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>20</td>
</tr>
</tbody>
</table>

α-Methylstyrene Polymerisation

<table>
<thead>
<tr>
<th>Sample ref.</th>
<th>α-methylstyrene (% wt. total monomer feed)</th>
<th>THF (% vol. total solvent)</th>
<th>Polymerisation</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>time (hours)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>temp. (°C)</td>
</tr>
<tr>
<td>S1</td>
<td>42.9</td>
<td>42.8</td>
<td>20.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>-20</td>
</tr>
<tr>
<td>S2</td>
<td>30.8</td>
<td>50.0</td>
<td>13.3</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>-78</td>
</tr>
</tbody>
</table>
raised from 20 to 50°C for 1 to 2 hours. This was similar to the procedure used for samples G1 and G2. After polymerising the α-methylstyrene for 18 to 20 hours the living polymers were terminated and precipitated as mentioned for polyisoprene-g-polystyrene.

3.2.2.3 EPDM-g-polystyrene

EPDM (Nordel 1635, E.I. du Pont de Nemours and Co.), with an ethylene content of 60% wt. and diene content of 4% wt., was used as the preformed polymer backbone from which to graft polystyrene. The EPDM was purified by first dissolving in cyclohexane (10% w/v solution), filtered to remove gel, and then washed several times with dilute nitric acid (0.1 M) and distilled water. The polymer was precipitated from solution using 2-propanol and then dried in a vacuum oven to constant weight (approx. 48 hours at 70°C). A sample of the purified EPDM (6.0 g) was placed in a reaction vessel similar to that used for isoprene grafting under argon blanket (figure 3.3) and then evacuated until a constant vacuum was obtained (approx. 30 minutes). Dried cyclohexane (250 cm³) was then distilled into the reactor and on thawing the solution stirred by magnetic follower until all the polymer had dissolved (approx. 6 hours). The transfer procedures for s-BuLi, TMEDA and styrene were then followed as for isoprene grafting under argon blanket (see section 3.2.2). The addition of s-BuLi (2.4 x 10⁻⁴ moles) and TMEDA (6.7 x 10⁻³ moles) to the reactor caused the solution to turn a bright yellow colour, indicating the formation of the metalation complex. After 3 hours a sample (5 cm³) was extracted for g.p.c. analysis and then styrene (3.5 g) syringed into the reactor. A deep red colouration formed in the solution. Stirring was continued for a further 19 hours before the reaction was terminated with a few drops of 2-propanol and the product precipitated out with excess alcohol and dried as mentioned earlier. A small portion of product (< 0.1 g) was used for g.p.c. analysis.
No discernable differences in the g.p.c. traces of the starting material, metalated polymer and final product could be found. There was, however, a very small homopolymer peak in the final product g.p.c. trace but this did not account for the 32% yield value obtained for the conversion of styrene to polymer. The apparent insensitivity of the g.p.c. trace to possible grafting can be attributed to the initial broad distribution of the starting material. From g.p.c., $\bar{M}_n^* = 140,000$, $\bar{M}_w^* = 360,000$ and hence $\frac{\bar{M}_w^*}{\bar{M}_n^*} = 2.6$ (where $\bar{M}_w^*$ and $\bar{M}_n^*$ are the molecular weights given as polystyrene equivalents, as mentioned in section 3.5.2.3). Although EPDM was considered a suitable backbone polymer for anionic grafting because of its low unsaturation and hence good ageing properties, the initial broad molecular weight distribution suggests that it would be better to monitor grafting effects with a backbone polymer having a narrower distribution. No further work was therefore carried out on EPDM.
3.3 PREPARATION OF HOMOPOLYMERS

To obtain background information on the grafting polymers, homopolymers of polystyrene, poly(\(\alpha\)-methylstyrene) and poly(vinyltoluene) were prepared under various experimental conditions and in several different solvents. All reagents were dried using the high vacuum techniques described in section 3.1.1 and polymerisations carried out using argon blanket methods similar to those mentioned in section 3.2.2. No major viscosity changes were noticeable during any of the preparations.

3.3.1 Polystyrene

The samples prepared and the experimental conditions employed are given in table 3.3. The transfer of monomer and solvent to the reactor was described in section 3.2.2. Similar methods were also used for the addition of initiator (s-BuLi) and TMEDA, when used. The initiator was added to the monomer solution in a single amount, this caused an immediate deep red colour to form when cyclohexane was the solvent and a pink or light red colour to form when THF was the solvent. During the polymerisation period considerable colour fading was noticeable in this latter solvent. All reactions were carried out at room temperature (20\(^{\circ}\)C). At the end of the designated polymerisation period the reaction was terminated with sufficient 2-propanol to just turn the solution colourless. To avoid reactions of the type given in equations (2.24) and (2.25) occurring as the result of small amounts of carbon dioxide being present in the alcohol, argon or dry nitrogen was bubbled through the 2-propanol for several minutes prior to use. It has also been suggested (207) that the presence of oxygen can lead to coupled polymer and therefore the purging of the alcohol with these 'inert' gases was considered essential if narrow distribution polymers were to be obtained. The polymer was precipitated from solution by pouring into a large excess (x 4) amount of alcohol (methanol or 2-propanol). If the precipitate did not coagulate
## TABLE 3.3

Experimental Conditions for the Preparation of Polystyrene and Poly(vinyltoluene)

<table>
<thead>
<tr>
<th>Sample reference</th>
<th>Monomer</th>
<th>Solvent</th>
<th>Concentration (% w/v)</th>
<th>s-Buli (moles/10^-5 g monomer)</th>
<th>Molar ratio [THEDAI]/[s-Buli]</th>
<th>Polymerisation time (hours)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H2</td>
<td>Styrene</td>
<td>THF</td>
<td>5.6</td>
<td>11.5</td>
<td></td>
<td>24.0</td>
</tr>
<tr>
<td>H3</td>
<td>Styrene</td>
<td>THF</td>
<td>3.0</td>
<td>9.1</td>
<td>9.4</td>
<td>24.0</td>
</tr>
<tr>
<td>H4</td>
<td>Styrene</td>
<td>Cyclohexane</td>
<td>1.0</td>
<td>41.7</td>
<td>13.1</td>
<td>25.8</td>
</tr>
<tr>
<td>H13</td>
<td>Vinyltoluene</td>
<td>THF</td>
<td>5.1</td>
<td>8.3</td>
<td></td>
<td>16.2</td>
</tr>
</tbody>
</table>
on stirring it was allowed to settle and then the supernatant liquid carefully decanted off. The polymer was then dried in a vacuum oven at 60 to 80°C for 24 hours or for longer periods if weight changes were still detectable after this time.

### 3.3.2 Poly(α-methylstyrene)

The various preparations carried out are listed in Table 3.4. All solvents and cosolvents were distilled into the reactor prior to monomer addition. The initiator (s-BuLi) and TMEDA, where used, were added at room temperature. This caused all the solutions to turn a characteristic red colour as mentioned above. Low temperature polymerisation was carried out as mentioned in section 3.2.2.2. The red colour persisted throughout the polymerisation period. To monitor the extent of the reaction on a weight basis or by g.p.c, polymer samples (2 cm³), accurately measured by syringe, were periodically removed from the reactor and added direct to an excess of 2-propanol which had been treated with argon or dry nitrogen as mentioned above. The precipitate obtained for each sample was transferred to a preweighed sample tube and then dried under vacuum at 60 to 80°C for as long as was required to produce no further weight changes (approx. 10 hours). All samples were cooled to room temperature under vacuum prior to reweighing. Termination, precipitation and sample recovery of the final product was carried out as mentioned in section 3.3.1.

### 3.3.3 Poly(vinyltoluene)

Vinyltoluene is the trivial name for ortho, meta and para substituted methylstyrene. The monomer used in the present work was a mixture of the meta (40%) and para (60%) isomers, however to distinguish it from α-methylstyrene it is simply referred to as vinyltoluene. A single poly(vinyltoluene) preparation was carried out, the experimental conditions
**TABLE 3.4**

Experimental Conditions for the Preparation of Poly(α-methylstyrene)

<table>
<thead>
<tr>
<th>Sample reference</th>
<th>Solvent system (% vol. cosolvent(s) given in brackets)</th>
<th>monomer conc. (% w/v)</th>
<th>s-Buli (moles/g monomer)</th>
<th>molar ratio [THEDA]/[s-Buli]</th>
<th>Polymerisation temp. (°C)</th>
<th>time (hours)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H5</td>
<td>Methylcyclohexane</td>
<td>0.9</td>
<td>14.1</td>
<td>5.1</td>
<td>-78</td>
<td>18.0</td>
</tr>
<tr>
<td>H6</td>
<td>Methylcyclohexane/cyclohexane (41.0)</td>
<td>1.4</td>
<td>6.5</td>
<td>6.3</td>
<td>-78</td>
<td>22.0</td>
</tr>
<tr>
<td>H7</td>
<td>THF</td>
<td>7.2</td>
<td>7.8</td>
<td>—</td>
<td>-45</td>
<td>6.5</td>
</tr>
<tr>
<td>H8</td>
<td>THF</td>
<td>6.8</td>
<td>8.4</td>
<td>—</td>
<td>-45</td>
<td>6.5</td>
</tr>
<tr>
<td>H9</td>
<td>Cyclohexane/THF (59.0)</td>
<td>6.2</td>
<td>5.0</td>
<td>—</td>
<td>-35</td>
<td>5.0</td>
</tr>
<tr>
<td>H10</td>
<td>Methylcyclohexane/THF (24.6)</td>
<td>0.7</td>
<td>34.1</td>
<td>5.4</td>
<td>-78</td>
<td>18.6</td>
</tr>
<tr>
<td>H11</td>
<td>Methylcyclohexane/cyclohexane (36.5)/THF (4.5)</td>
<td>1.3</td>
<td>6.4</td>
<td>5.7</td>
<td>-78</td>
<td>56.0</td>
</tr>
<tr>
<td>H12</td>
<td>Methylcyclohexane/cyclohexane (42.0)/THF (9.1)</td>
<td>1.7</td>
<td>6.4</td>
<td>5.7</td>
<td>-78</td>
<td>44.0</td>
</tr>
</tbody>
</table>
for which are given in table 3.3. The preparation carried out in THF at 20°C showed similar colour changes to those encountered with the styrene systems, i.e. the solution turned a light red colour on initiation but which faded after several hours. A sample (2 cm$^3$), extracted 1.5 hours after initiation, was precipitated and dried and then analysed by g.p.c. Termination and product recovery were the same as in the polystyrene and poly($\alpha$-methylstyrene) preparations.
3.4 METALATION AND GRAFTING OF SBR

An anionically prepared commercial SBR, Solprene 1204 (Phillips Petroleum Ltd.), with a narrow molecular weight distribution was chosen as the preformed polymer on which to carry out grafting reactions using a metalation technique similar to that described for polyisoprene (section 3.2). Prior to use the SBR was first dissolved in cyclohexane (5% w/v solution), filtered to remove gel, and then solvent cast at room temperature on sheets of aluminium foil. To extract the last traces of solvent the SBR was dried to constant weight in a vacuum oven at 60°C. The rubber was then stored in a vacuum dessicator over silica gel until required. All reagents used in the preparations were dried using the high vacuum methods described in section 3.1.1. The reactions were carried out using the argon blanket techniques outlined in section 3.2.2.

3.4.1 Metalation Procedure

The general method for the metalation of SBR was as follows. An accurately weighed amount of dried SBR (1.5-10 g) was placed in a graduated reaction vessel (figure 3.3) fitted with greaseless tap and rubber septum and containing a glass covered magnetic follower. This was then attached to the vacuum line and evacuated for several hours. To check for possible sample weight loss the evacuated flask was periodically removed from the vacuum line and reweighed. No detectable changes were observed in any of the preparations and it was therefore assumed that all solvent and moisture had been removed during vacuum oven drying. Solvent (see individual preparations for the solvent(s) used) was vacuum distilled from a storage flask into the reaction vessel containing the SBR. The solution was then stirred until all the polymer had dissolved (approx. 6 hours). The solution concentration was kept below 5% w/v to avoid stirring problems at higher concentrations as a result of the increased viscosity. (All solution concentrations quoted refer to metalation solution.) The reactor
and the various collection flasks containing the monomer and TMEDA were then filled with argon as mentioned in section 3.2.2. Early studies of the metalation of SBR with the s-BuLi-TMEDA complex in non-polar solvents had shown that upon metalation the polymer solution turned a deep red colour. This colour indication of a 'living' system was used as a guide in determining the point at which initiator ceased to be deactivated by impurities or side reactions. First the TMEDA was added to the solution using the syringe technique mentioned earlier (section 3.2.1.1) and then initiator (s-BuLi) was added dropwise until the solution just turned a permanent straw yellow colour upon vigorous stirring. This was then taken as the point at which a living system just started to form. A further calculated amount of initiator was added and the solution turned a bright red colour. This second quantity of initiator was the amount of 'active' initiator employed in the reaction. Unless where otherwise stated only 'active' amounts of s-BuLi are quoted throughout. The solution was then stirred for 2 to 28 hours at 20°C or 50°C. Temperature is only quoted where metalations were not performed at 20°C. At the end of this metalation period a small sample (2 - 10 cm³) was removed, terminated and precipitated in 2-propanol (argon purged as mentioned in section 3.3.1), and then dried for g.p.c. analysis. Metalated SBR was then used to prepare the following graft copolymers: SBR-g-polystyrene, SBR-g-poly(α-methylstyrene), SBR-g-poly(α-methylstyrene-co-styrene) and SBR-g-poly(vinyltoluene). Several samples were prepared in which no monomer was added, instead the metalated polymers were treated with several different terminating agents: 2-propanol, deuterium oxide and carbon dioxide.

3.4.2 Preparation of SBR-g-polystyrene

Three different solvent systems were used: cyclohexane, THF and methylcyclohexane/THF.
The experimental conditions for the grafting of SBR with styrene in cyclohexane are given in table 3.5. Styrene was added to the metalated SBR in a similar manner to that described for metalated polyisoprene (section 3.2). The solution remained a deep red colour during the styrene addition. Similar viscosity changes to those observed with the polyisoprene-g-polystyrene preparation (section 3.2.1) were observed, i.e. viscosity increased during metalation and as styrene was added it decreased slightly, then as the polymerisation proceeded the viscosity gradually began to increase again. In several cases (G10, G18 and G19) stirring of the solutions was only just possible during metalation and polymerisation. Styrene polymerisation was carried out for 8 to 27 hours at 20°C. During this period if samples were taken (2 or 5 cm³) the procedure for their extraction was identical to that mentioned in section 3.2.2. At the end of the polymerisation period termination was carried out as described in section 3.3.1. The change from a deep red to a colourless solution was accompanied by a considerable drop in viscosity as indicated by the increased activity of the magnetic follower. Product recovery was identical to the procedure outlined in section 3.3.1. Thorough drying of product was required to ensure accurate values of product yield and grafting efficiency (see section 4.5) could be obtained.

THF

The preparation of an SBR-g-polystyrene copolymer in a polar solvent was attempted using THF as the solvent. The experimental conditions for this one attempt are given in table 3.6. Using the same procedure as above for cyclohexane it was found that the solution did not turn a distinctive yellow colour on s-BuLi.TMEDA addition, nor a deep red colour on further s-BuLi addition. There are two possible
### Table 3.5

**Reaction Conditions for the Preparation of SBR-g-polystyrene in cyclohexane**

<table>
<thead>
<tr>
<th>Sample Reference</th>
<th>SBR Conc. (% w/v)</th>
<th>s-BuLi[^a](mol/10^{-5} g SBR)</th>
<th>Molar Ratio [TMEDA]/[s-BuLi]</th>
<th>Metalation Time (hours)</th>
<th>Styrene (% wt. total SBR + monomer)</th>
<th>Polymerisation Time (hours)</th>
</tr>
</thead>
<tbody>
<tr>
<td>G10</td>
<td>3.9</td>
<td>7.3[^b]</td>
<td>9.2</td>
<td>5.0</td>
<td>33.6</td>
<td>18.0</td>
</tr>
<tr>
<td>G11</td>
<td>1.6</td>
<td>16.0</td>
<td>8.3</td>
<td>14.0</td>
<td>29.9</td>
<td>27.0</td>
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<td>8.3</td>
<td>14.5</td>
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<td>27.0</td>
</tr>
<tr>
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<td>8.3</td>
<td>14.5</td>
<td>49.2</td>
<td>27.0</td>
</tr>
<tr>
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<td>1.2</td>
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<td>2.0</td>
<td>39.4</td>
<td>8.3</td>
</tr>
<tr>
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<td>11.8</td>
<td>11.1</td>
<td>17.0</td>
<td>39.5</td>
<td>8.3</td>
</tr>
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<td>5.0</td>
<td>39.5</td>
<td>8.3</td>
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<td>12.8</td>
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<td>12.8</td>
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<td>11.0</td>
</tr>
<tr>
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<td>15.0</td>
<td>12.8</td>
<td>38.6</td>
<td>11.0</td>
</tr>
<tr>
<td>G21</td>
<td>1.5</td>
<td>7.9</td>
<td>50.0</td>
<td>12.8</td>
<td>39.8</td>
<td>11.0</td>
</tr>
</tbody>
</table>

---

[^a]: Unless where otherwise mentioned 'active' initiator amounts only are quoted throughout.

[^b]: Total initiator added.
**TABLE 3.6**

Reaction Conditions for the Attempted Preparation of SBR-g-Polystyrene in THF and methylcyclohexane/THF

<table>
<thead>
<tr>
<th>Sample reference</th>
<th>Solvent(s)</th>
<th>SBR conc. (% w/v)</th>
<th>S-BuLi (moles/10^-5 g SBR)</th>
<th>Molar ratio [THFEDA] /[s-BuLi]</th>
<th>Metalation time (hours)</th>
<th>Styrene (% wt. total SBR + monomer)</th>
<th>Polymerisation time (hours)</th>
</tr>
</thead>
<tbody>
<tr>
<td>G22</td>
<td>THF</td>
<td>1.3</td>
<td>31.0(^b)</td>
<td>25.1</td>
<td>5.0</td>
<td>47.3</td>
<td>8.5</td>
</tr>
<tr>
<td>G23</td>
<td>Methylcyclohexane/THF (14.0(^a))</td>
<td>1.9</td>
<td>11.5</td>
<td>50.0</td>
<td>14.0</td>
<td>31.2</td>
<td>16.0(^c)</td>
</tr>
</tbody>
</table>

\(^a\) % vol. cosolvent

\(^b\) Total initiator used

\(^c\) THF added after 5.5 hours.
reasons for this, either the complex and metalated polymer did not form coloured solutions in this polar medium or the initiator had been deactivated by impurities present in the solution. In an attempt to eliminate this latter possibility, further quantities of s-BuLi and TMEDA were added. A very faint orange colouration formed in the solution, which did not change in colour or intensity after further additions of the two reagents. The addition of styrene caused the solution to turn a very faint pink colour, which after 3 hours had turned colourless. A sample (5 cm$^3$) was removed for g.p.c. analysis and then an additional quantity of initiator added to the reactor. The pink colouration returned and the solution was stirred for a further 5.5 hours. At the end of this polymerisation period the colour was still present. Termination and sample recovery were carried out as mentioned in section 3.3.1. No viscosity changes were noticeable throughout the preparation.

**Methylcyclohexane/THF**

The experimental conditions for the one preparation are given in table 3.6. The metalation reaction was carried out in methylcyclohexane only. The addition of s-BuLi and TMEDA produced a similar colour change to that found with cyclohexane. Similar viscosity changes were also observed. After a sample (5 cm$^3$) had been extracted at the end of the metalation period and used for g.p.c. analysis, styrene was added and allowed to polymerise for 5.5 hours. A second sample (5 cm$^3$) was then removed prior to the addition of THF via the argon pressurisation method described in section 3.2.2.2. No colour or viscosity changes were noticeable on THF addition. After periodic sampling the reaction was terminated after 16 hours. Termination, precipitation and sample drying were performed as before (section 3.3.1).
3.4.3 SBR-g-poly(α-methylstyrene)

To ensure appreciable conversion of α-methylstyrene to polymer, all polymerisations were carried out in the temperature range -35 to -78°C using the two low temperature bath methods mentioned in section 3.2.2.2. Several different solvent systems were used: THF, methylcyclohexane, methylcyclohexane/cyclohexane, cyclohexane/THF, methylcyclohexane/THF and methylcyclohexane/cyclohexane/THF. Unless otherwise stated, all sample extractions, precipitations and drying procedures were carried out as mentioned in sections 3.3.1 and 3.3.2.

THF

The experimental conditions are given in table 3.7. Large quantities of initiator were required to achieve solution colouration during metalation. The ill-defined colour obtained was similar to that encountered with the attempted styrene grafting of SBR in THF (section 3.4.2). Colour fading and the lack of viscosity changes were also similar features.

Methylcyclohexane

The experimental conditions are given in table 3.7. Each preparation gave a bright red solution on metalation and which remained unchanged during and after α-methylstyrene addition. Monomer was added at room temperature and then the reactor placed in the appropriate low temperature bath. Preparation G29 was run at -35°C for 24 hours and then at -78°C for 72 hours, with samples taken for g.p.c. analysis at the end of each temperature period.

Methylcyclohexane/cyclohexane

See methylcyclohexane/cyclohexane/THF preparations.
## TABLE 3.7

Reaction Conditions for the Attempted Preparation of SBR-g-(α-methylstyrene) in THF and methylcyclohexane

<table>
<thead>
<tr>
<th>Sample ref.</th>
<th>SBR conc. (% w/v)</th>
<th>s-BuLi (molecules/10^3 g SBR)</th>
<th>molar ratio [TMEDA]/[s-BuLi]</th>
<th>metalation time (hours)</th>
<th>α-methylstyrene (% wt. total SBR + monomer)</th>
<th>Polymerisation time (hours)</th>
<th>temp. (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>THF</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>G24</td>
<td>2.1</td>
<td>23.2&lt;sup&gt;a&lt;/sup&gt;</td>
<td>8.6</td>
<td>5.0</td>
<td>48.3</td>
<td>7.0</td>
<td>-40</td>
</tr>
<tr>
<td>G25</td>
<td>1.5</td>
<td>40.8&lt;sup&gt;a&lt;/sup&gt;</td>
<td>5.4</td>
<td>4.0</td>
<td>53.8</td>
<td>20.0</td>
<td>-45</td>
</tr>
<tr>
<td>G26</td>
<td>1.1</td>
<td>62.3&lt;sup&gt;a&lt;/sup&gt;</td>
<td>1.7</td>
<td>17.5</td>
<td>38.3</td>
<td>0.9</td>
<td>-35</td>
</tr>
<tr>
<td>Methylcyclohexane</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>G27</td>
<td>2.0</td>
<td>60.2</td>
<td>8.2</td>
<td>18.0</td>
<td>40.4</td>
<td>8.0</td>
<td>-35</td>
</tr>
<tr>
<td>G28</td>
<td>1.4</td>
<td>23.9</td>
<td>20.7</td>
<td>18.0</td>
<td>40.4</td>
<td>24.0</td>
<td>-78</td>
</tr>
<tr>
<td>G29</td>
<td>1.5</td>
<td>14.3</td>
<td>30.7</td>
<td>18.0</td>
<td>37.8</td>
<td>24.0</td>
<td>-35</td>
</tr>
</tbody>
</table>

<sup>a</sup> Total initiator used
The experimental conditions are given in Table 3.8. As with the styrene grafting of SBR in a mixed solvent system the THF was introduced after the monomer addition. In all preparations the red metalation colour persisted throughout the metatation and polymerisation periods, turning only slightly lighter on THF addition. It was difficult to ascertain whether this was due to a number of 'active' sites being 'killed off' or to a dilution effect as a result of the increased volume. The viscosity also decreased on THF addition. During polymerisation the viscosity began to increase again, however, this may have been a consequence of carrying out the reaction at low temperature rather than due to chain association effects.

To follow the extent of reaction on a weight basis or by g.p.c., periodic sampling (2 or 5 cm$^3$), accurately measured by syringe, was carried out. The samples were then either precipitated as mentioned in section 3.3.2 or added to a very small amount (1 cm$^3$) of THF (argon purged, as mentioned for 2-propanol, section 3.3.2). Because the THF was undried it was sufficiently 'wet' to terminate the polymer samples as soon as they were added. In all cases where a 'living' sample was removed from the reactor contact with the atmosphere prior to termination was avoided because of possible coupling reactions with oxygen (207) or with carbon dioxide as mentioned in section 2.1.3. The THF samples were dried to constant weight in the same way as the precipitated samples (see section 3.3.2).

The minimum amounts of THF used in the cyclohexane/THF system were determined by the freezing point of the mixture for that particular polymerisation temperature, i.e. at -35°C the minimum amount of THF required was 23% vol. total solvent and for temperatures down to -78°C the amount required was 40% vol. total solvent.
<table>
<thead>
<tr>
<th>Sample ref.</th>
<th>SBR conc. (% w/v)</th>
<th>s-BuLi (mols/10^-3 g SBR)</th>
<th>molar ratio [TMEDA]/[s-BuLi]</th>
<th>metalation time (hours)</th>
<th>α-methylstyrene (% wt. total SBR + monomer)</th>
<th>THF (% vol. total solvent)</th>
<th>Polymerisation time (hours)</th>
<th>temp. (°C)</th>
</tr>
</thead>
<tbody>
<tr>
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<td>33.3</td>
<td>4.5</td>
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<td>-47</td>
</tr>
<tr>
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<td>11.5</td>
<td>37.0</td>
<td>17.5</td>
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<td>20.0</td>
<td>-35</td>
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<td>14.0</td>
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<td>17.5</td>
<td>-35</td>
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<tr>
<td>G33</td>
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<td>5.9</td>
<td>74.0</td>
<td>18.5</td>
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<td>40.7</td>
<td>9.0</td>
<td>-35</td>
</tr>
<tr>
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<td>11.8</td>
<td>55.0</td>
<td>16.0</td>
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<td>24.3</td>
<td>20.8</td>
<td>-35</td>
</tr>
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<td>16.0</td>
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<td>48.4</td>
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<td>-35</td>
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<td>5.0^a</td>
<td>40.6</td>
<td>61.0</td>
<td>18.0</td>
<td>-78</td>
</tr>
</tbody>
</table>

a) Metalation at 50°C.
Methylcyclohexane/THF

The experimental conditions are given in table 3.9. THF was added after monomer addition. Similar colour and viscosity changes to those obtained in the above system were observed. Because methylcyclohexane has a freezing point of -126°C there was no lower limit to the amount of THF that could be used. Sampling and product recovery were carried out as for the cyclohexane/THF systems.

Methylcyclohexane/cyclohexane/THF

The experimental conditions are given in table 3.10. Metalation was carried out in methylcyclohexane/cyclohexane and then THF introduced after α-methylstyrene addition. In one preparation (G56) no THF was used, however because it was part of a group of experiments (G55 - G58) it is tabulated here rather than in a separate section.

3.4.4 SBR-g-poly(α-methylstyrene-co-styrene)

In all preparations both monomers were added to the reactor together. Styrene was present as 10 to 50% wt. total monomer feed. Similar solvent systems to those described in the preceding sections were used, i.e. methylcyclohexane, methylcyclohexane/cyclohexane, cyclohexane/THF, methylcyclohexane/THF and methylcyclohexane/cyclohexane/THF. The experimental conditions employed for the preparations in these solvents are given in tables 3.11 and 3.12. Solution colouration and viscosity changes were as found in section 3.4.3. In addition to periodic sampling during the grafting reaction, samples were also taken at the end of each temperature period if more than one polymerisation temperature was used.
<table>
<thead>
<tr>
<th>Sample ref.</th>
<th>SBR conc. (% w/v)</th>
<th>s-Buli (moles/10^-5 g SBR)</th>
<th>molar ratio [TMEDA]</th>
<th>Metalation time (hours)</th>
<th>α-methylstyrene (% wt. total SBR + monomer)</th>
<th>THF (% vol. total solvent)</th>
<th>Polymerisation time (hours)</th>
<th>Temp. (°C)</th>
</tr>
</thead>
<tbody>
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<td>50.0</td>
<td>-78</td>
</tr>
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<td>27.0</td>
<td>22.5</td>
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<td>36.4</td>
<td>50.0</td>
<td>-78</td>
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<td>14.5</td>
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<td>-78</td>
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<td>9.1</td>
<td>21.4</td>
<td>-78</td>
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<td>5.5</td>
<td>14.5</td>
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<td>9.1</td>
<td>21.2</td>
<td>-48</td>
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<td>-78</td>
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<td>37.6</td>
<td>26.8</td>
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<td>19.0</td>
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<td>20.8</td>
<td>-78</td>
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<td>-78</td>
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<td>-78</td>
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<td>5.6</td>
<td>19.0</td>
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<td>38.8</td>
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<td>-78</td>
</tr>
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<td>0.9</td>
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<td>26.3</td>
<td>23.9</td>
<td>-78</td>
</tr>
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<td>3.8</td>
<td>28.3</td>
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<td>-78</td>
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<td>-48</td>
</tr>
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<td>33.6</td>
<td>27.7</td>
<td>23.8</td>
<td>-35</td>
</tr>
</tbody>
</table>

<sup>a</sup) Metalated at 50°C.
TABLE 3.10

Reaction Conditions for the Preparation of SBR-g-poly(α-methylstyrene) in Methylocyclohexane/cyclohexane\(^a\) with and without THF present

<table>
<thead>
<tr>
<th>Sample ref.</th>
<th>SBR conc. (% w/v)</th>
<th>s-BuLi (moles/10(^{-5}) g SBR)</th>
<th>molar ratio [TMEDA]/[s-BuLi]</th>
<th>metalation time (hours)</th>
<th>α-methylstyrene (% wt. total SBR + monomer)</th>
<th>THF (% vol. total solvent)</th>
<th>Polymerisation</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
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</tr>
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<td>10.0</td>
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<td>15.0</td>
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</tr>
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<td>9.5</td>
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<td>15.0</td>
<td>38.1</td>
<td>9.1</td>
<td>30.0</td>
</tr>
</tbody>
</table>

\(^{a}\) 50/50 mixture.
### TABLE 3.11

Reaction Conditions for the Preparation of SBR-g-poly(α-methylstyrene-co-styrene) in cyclohexane/THF

<table>
<thead>
<tr>
<th>Sample ref.</th>
<th>SBR conc. (% w/v)</th>
<th>s-BuLi (mole/10^-5 g SBR)</th>
<th>molar ratio [s-BuLi] [TMEDA]</th>
<th>metalation time (hours)</th>
<th>monomer (% wt. total SBR + monomer)</th>
<th>styrene (% wt. total monomer)</th>
<th>THF (% vol. total solvent)</th>
<th>Polymerisation time (hours)</th>
<th>Polymerisation temp. (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>G64</td>
<td>1.6</td>
<td>7.9</td>
<td>13.8</td>
<td>14.0</td>
<td>33.7</td>
<td>29.0</td>
<td>45.7</td>
<td>2.0</td>
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<tr>
<td></td>
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<td></td>
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<td></td>
<td></td>
<td></td>
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<td></td>
<td>18</td>
</tr>
<tr>
<td>G65</td>
<td>1.2</td>
<td>7.9</td>
<td>8.3</td>
<td>12.0</td>
<td>28.6</td>
<td>26.2</td>
<td>37.7</td>
<td>3.0</td>
<td>20</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>13</td>
</tr>
<tr>
<td>G66</td>
<td>1.4</td>
<td>7.9</td>
<td>8.3</td>
<td>12.0</td>
<td>29.8</td>
<td>50.0</td>
<td>32.1</td>
<td>4.0</td>
<td>20</td>
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<td>G67</td>
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<td>8.1</td>
<td>13.8</td>
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<td>50.0</td>
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<td>G68</td>
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<td>37.0</td>
<td>19.0</td>
<td>48.7</td>
<td>18.6</td>
<td>33.3</td>
<td>8.0</td>
<td>-78</td>
</tr>
</tbody>
</table>

* a) Prior to THF addition.*
### TABLE 3.12

**Reaction Conditions for the Preparation of SBR-g-poly(α-methylstyrene-co-styrene) in Various Solvents**

<table>
<thead>
<tr>
<th>Sample ref.</th>
<th>SBR conc. (% w/v)</th>
<th>s-Buli (moles/10^−5 g SBR)</th>
<th>molar ratio [TMEDA]/[s-Buli]</th>
<th>metatation time (hours)</th>
<th>monomer (% wt. total SBR + monomer)</th>
<th>styrene (% wt. total monomer)</th>
<th>THF (% vol. total solvent)</th>
<th>Polymerisation time (hours)</th>
<th>temp. (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>G61</td>
<td>1.4</td>
<td>16.0</td>
<td>40.0</td>
<td>13.0</td>
<td>61.7</td>
<td>13.6</td>
<td></td>
<td>6.0</td>
<td>-38</td>
</tr>
<tr>
<td>G62</td>
<td>1.3</td>
<td>16.8^b</td>
<td>19.9</td>
<td>9.0</td>
<td>52.7</td>
<td>10.1</td>
<td></td>
<td>13.5</td>
<td>-40</td>
</tr>
<tr>
<td>G63</td>
<td>1.6</td>
<td>20.3^b</td>
<td>18.8</td>
<td>18.0</td>
<td>56.4</td>
<td>38.6</td>
<td></td>
<td>8.0</td>
<td>-35</td>
</tr>
<tr>
<td>G69</td>
<td>1.8</td>
<td>13.3</td>
<td>5.5</td>
<td>14.5^c</td>
<td>35.7</td>
<td>18.2</td>
<td>9.1</td>
<td>20.9</td>
<td>-78</td>
</tr>
<tr>
<td>G70</td>
<td>2.1</td>
<td>14.3^b</td>
<td>22.2</td>
<td>8.0</td>
<td>50.1</td>
<td>15.6</td>
<td>20.0</td>
<td>13.2</td>
<td>-33</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Sample ref.</th>
<th>SBR conc. (% w/v)</th>
<th>s-Buli (moles/10^−5 g SBR)</th>
<th>molar ratio [TMEDA]/[s-Buli]</th>
<th>metatation time (hours)</th>
<th>monomer (% wt. total SBR + monomer)</th>
<th>styrene (% wt. total monomer)</th>
<th>THF (% vol. total solvent)</th>
<th>Polymerisation time (hours)</th>
<th>temp. (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methylecylcyclohexane</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Methylecylcyclohexane/cyclohexane</td>
<td>G61</td>
<td>1.4</td>
<td>16.0</td>
<td>40.0</td>
<td>13.0</td>
<td>61.7</td>
<td>13.6</td>
<td>6.0</td>
<td>-38</td>
</tr>
<tr>
<td>Methylecylcyclohexane/cyclohexane</td>
<td>G62</td>
<td>1.3</td>
<td>16.8^b</td>
<td>19.9</td>
<td>9.0</td>
<td>52.7</td>
<td>10.1</td>
<td>13.5</td>
<td>-40</td>
</tr>
<tr>
<td>Methylecylcyclohexane/cyclohexane</td>
<td>G63</td>
<td>1.6</td>
<td>20.3^b</td>
<td>18.8</td>
<td>18.0</td>
<td>56.4</td>
<td>38.6</td>
<td>8.0</td>
<td>-35</td>
</tr>
<tr>
<td>Methylecylcyclohexane/THF</td>
<td>G69</td>
<td>1.8</td>
<td>13.3</td>
<td>5.5</td>
<td>14.5^c</td>
<td>35.7</td>
<td>18.2</td>
<td>20.9</td>
<td>-78</td>
</tr>
<tr>
<td>Methylecylcyclohexane/cyclohexane/THF</td>
<td>G70</td>
<td>2.1</td>
<td>14.3^b</td>
<td>22.2</td>
<td>8.0</td>
<td>50.1</td>
<td>15.6</td>
<td>13.2</td>
<td>-33</td>
</tr>
</tbody>
</table>

a) 50/50, methylecylcyclohexane/cyclohexane.
b) total initiator used.
c) metalated at 50°C.
3.4.5 SBR-g-poly(vinyltoluene)

Vinyltoluene was treated in a similar manner to styrene. Polymerisations were carried out at 20°C. Two solvent systems were used: THF and cyclohexane. The experimental conditions for the two preparations carried out are given in table 3.13. Colour and viscosity changes were identical to those found for the styrene grafting of SBR in these solvents.

3.4.6 Model Terminations of Metalated SBR

As mentioned in section 2.1.3 the introduction of functional groups into the structure of a living polymer can be readily achieved by reacting with a suitable terminating agent. It is therefore possible, in the case of metalated SBR, to add functional groups at the sites of lithiation. Three terminating agents were chosen: 2-propanol, deuterium oxide and carbon dioxide. Proton termination via 2-propanol was performed so that a comparison could then be made between unmetalated and metalated SBR to determine to what extent the metalation reaction was reversible. The intention of terminating with deuterium oxide and carbon dioxide was to place deuterium and carboxylic acid groups at each of the lithiated sites. Analytical techniques could then be used to determine the quantity and position of the active sites (see section 4.4.3).

3.4.6.1 Metalated SBR terminated with 2-propanol

Following the metalation procedures outlined in section 3.4.1 several metalated SBR polymers were prepared, the experimental conditions for which are given in table 3.14. To be able to compare results from the two solvents used the 'active' initiator (see section 3.4.1) in the THF preparations was taken from the point at which colouration was just detectable. The terminating agent 2-propanol was dried over molecular sieves for several days prior to use. To prevent possible coupling reactions occurring as the result of oxygen or carbon dioxide being
**TABLE 3.13**

Reaction Conditions for the Preparation of SBR-g-poly(vinyltoluene) in Various Solvents

<table>
<thead>
<tr>
<th>Sample ref.</th>
<th>SBR conc. (% w/v)</th>
<th>s-BuLi (moles/ $10^{-5}$ g SBR)</th>
<th>molar ratio [TMEDA] /[s-BuLi]</th>
<th>metatation time (hours)</th>
<th>vinyltoluene (% wt. total SBR + monomer)</th>
<th>Polymerisation time (hours)</th>
</tr>
</thead>
<tbody>
<tr>
<td>THF</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>G71</td>
<td>1.9</td>
<td>7.5&lt;sup&gt;a&lt;/sup&gt;</td>
<td>13.3</td>
<td>6.5</td>
<td>39.4</td>
<td>27.0</td>
</tr>
<tr>
<td>Cyclohexane</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>G72</td>
<td>2.2</td>
<td>5.5</td>
<td>10.2</td>
<td>5.5</td>
<td>37.5</td>
<td>72.0</td>
</tr>
</tbody>
</table>

<sup>a</sup> total initiator added.
TABLE 3.14

Reaction Conditions for the Metalation of SBR Samples used for Model Terminations with 2-propanol, Deuterium Oxide and Carbon Dioxide

<table>
<thead>
<tr>
<th>Sample ref.</th>
<th>Solvent</th>
<th>SBR conc. (% w/v)</th>
<th>S-BuLi (moles/10^-5 g SBR)</th>
<th>Molar ratio [TMEDA]/[s-BuLi]</th>
<th>Metalation time (hours)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-propanol</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>M1</td>
<td>THF</td>
<td>2.1</td>
<td>23.2</td>
<td>8.6</td>
<td>5.0</td>
</tr>
<tr>
<td>M2</td>
<td>THF</td>
<td>1.5</td>
<td>40.9</td>
<td>5.4</td>
<td>4.5</td>
</tr>
<tr>
<td>M3</td>
<td>Cyclohexane</td>
<td>1.4</td>
<td>35.0</td>
<td>20.7</td>
<td>18.2</td>
</tr>
<tr>
<td>M4</td>
<td>Cyclohexane</td>
<td>1.0</td>
<td>120.0</td>
<td>5.5</td>
<td>13.0</td>
</tr>
<tr>
<td>Deuterium Oxide</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>M5</td>
<td>Cyclohexane</td>
<td>0.8</td>
<td>136.8</td>
<td>4.9</td>
<td>16.3</td>
</tr>
<tr>
<td>Carbon Dioxide</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>M6</td>
<td>Cyclohexane</td>
<td>0.9</td>
<td>18.2</td>
<td>20.1</td>
<td>18.5</td>
</tr>
</tbody>
</table>
present in the alcohol the terminating agent was thoroughly purged with argon (as mentioned in section 3.3.1) before being added to the reaction vessel. The alcohol was added dropwise until the solution turned colourless, an excess amount was then added until a precipitate was just visible. Complete precipitation was performed as mentioned in section 3.3.1.

3.4.6.2 Metalated SBR terminated with deuterium oxide

The procedure was similar to that used in the above preparations. The experimental conditions for the SBR metalation are given in table 3.14.

Deuterium oxide (Aldrich, Gold Label, 99.8 atom % D) was used as supplied. An excess terminating quantity (1 cm$^3$) of deuterium oxide was added to the metalated SBR solution and then stirred vigorously until the deep red colouration disappeared (approx. 30 seconds). This long terminating period was due to the immiscibility of the deuterium oxide in the solvent, however vigorous agitation was sufficient to create the mixing necessary to induce termination.

3.4.6.3 Metalated SBR terminated with carbon dioxide

Metalation was carried out as mentioned above. The experimental conditions for the one preparation are given in table 3.14. The metalated SBR solution was then transferred by argon pressurisation (as mentioned for THF transfer, section 3.2.2.2) into a flask containing a solid carbon dioxide/THF (vacuum dried) slurry. Termination of the polymer solution occurred immediately on contact with the slurry. After warming to room temperature a small quantity (4 cm$^3$) of acidified methanol was added to the solution and the mixture thoroughly stirred. Precipitation was carried out in excess (x 4) acidified methanol. The precipitate was washed with distilled water, dried and then redissolved in THF. Reprecipitation from THF was achieved using excess methanol. The product was then recovered and dried as mentioned in section 3.3.1.
SECTION B: POLYMER CHARACTERISATION

3.5 GEL PERMEATION CHROMATOGRAPHY (G.P.C.)

3.5.1 Measuring Procedure

Gel permeation chromatography was used for the determination of molecular weights and molecular weight distributions of the polymers prepared. A Waters Associates ALC/GPC 501 instrument was used with two different sets of columns. The analysis of polyisoprene and EPDM polymers was carried out using four Styragel (40 µm particle size, Waters Associates) columns with quoted porosities of $10^3$, $10^4$, $10^5$, and $10^6$. The analysis of the SBR polymers was carried out using four macrogel (20 µm particle size, Polymer Laboratories) columns of quoted porosities $70$, $10^3$, $10^4$, and $10^5$. Using THF (stabilised with 0.2% w/v hydroquinone) as carrier solvent and a pumping rate of 2.5 cm$^3$ min$^{-1}$, complete chromatograms were obtained within 30 minutes. A Waters refractometer was used as the detector. Because a small injection loop (0.2 cm$^3$ capacity) was used, samples available in very small quantities could be analysed within the recommended solution concentrations (0.01 - 0.40% w/v THF). All samples were filtered through glass microfibre filters (Whatmans GF/A) before injection into the apparatus. The overall chromatogram path length was obtained using tetraphenylethylene (TPE, molecular weight 332) as the internal standard. TPE was present as 0.02 to 0.04% w/v THF in all polymer solutions. Retention/elution volume ($V_R$) was given as a percentage of the TPE path length (100% corresponded to 68.5 ± 0.5 cm$^3$ of eluent).

3.5.2 Calibration Procedures

The instrument was calibrated using polystyrene standards (Waters Associates) with narrow molecular weight distributions ($\bar{M}_w/\bar{M}_n < 1.1$). Taking the polystyrene standards' peak molecular weight as the calibration
molecular weight parameter ($M$) curves of log $M$ against retention volume ($V_R$, given as % TPE path length) for the two sets of columns used are given in figures 3.5 and 3.6.

### 3.5.2.1 StyrageL columns

The method used for the determination of the molecular weight characteristics of a polystyrene sample, using the StyrageL columns, is as follows:

a) a baseline is drawn across the g.p.c. trace of the unknown sample and then chromatogram height ($h_i$) measured at 1 or $\frac{1}{2}$% TPE path length ($V_R$) intervals across the trace,

b) a normalised elution curve is then constructed of $h_i/\Sigma h_i$ against $V_R$, with the ordinate of this curve corresponding to $dw/dV_R$ (see section 2.4.2),

c) from the calibration curve (fig. 3.5) a range of values for $d(\log M)/dV_R$ and $M$ for the same values of $V_R$ is obtained,

d) using equation (2.44) a normalised weight differential molecular weight distribution curve can be constructed,

e) $\bar{M}_w$, $\bar{M}_n$ and $M_p$ can then be determined using equations (2.45), (2.46) and (2.47). To reduce the number of manual calculations a computer program based on the method of Pickett et al. (208) and modified by Croucher (209) was used.

### 3.5.2.2 Macrogel columns

Because the polystyrene calibration trace for the Macrogel columns showed remarkably good straight line correlation between log $M$ and % TPE path length over the particular molecular weight range of interest ($\log M = 3.0 - 5.0$) a simplified version of the above procedure could be used. Assuming detector response is proportional to sample concentration, i.e. $h_i \propto Ni$, then using equations (2.38) and (2.39) we can obtain expressions
FIGURE 3.5
Polystyrene calibration curve for Styrage columns

LOG M

COUNTS ($V_R$ as % TFE path length)
FIGURE 2.6
Polystyrene calibration curve for Macrogel columns

LOG M

COUNTS (\(V_R\) as % TPE path length)
for $\overline{M}_w$ and $\overline{M}_n$ in the form of

$$\overline{M}_w = \frac{\sum M_i n_i}{\sum n_i} \quad (3.1)$$

$$\overline{M}_n = \frac{\sum n_i}{\sum (n_i / M_i)} \quad (3.2)$$

Values for $M_p$ were determined as before using equation (2.47). A computer program (210) was used for the calculation of the molecular weight averages given in the above equations.

3.5.2.3 Universal calibrations

In the absence of standards for the calibration of polymers other than polystyrene, a universal calibration procedure was adopted (section 2.4.3). To convert polystyrene equivalent molecular weight values for polyisoprene to true values, equation (2.53) was used. Values of $[\langle r_o^2 \rangle / \langle M \rangle]^{1/2}$ are given in table 3.15.

**Table 3.15**

<table>
<thead>
<tr>
<th>Polymer</th>
<th>$[\langle r_o^2 \rangle / \langle M \rangle]^{1/2} \times 10^4$ nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>polystyrene</td>
<td>670</td>
</tr>
<tr>
<td>cis-1,4-polyisoprene</td>
<td>810</td>
</tr>
<tr>
<td>trans-1,4-polyisoprene</td>
<td>970</td>
</tr>
<tr>
<td>poly(1-pentene)</td>
<td>801</td>
</tr>
<tr>
<td>poly($\alpha$-methylstyrene)</td>
<td>655</td>
</tr>
<tr>
<td>poly(2,4-dimethylstyrene)</td>
<td>640</td>
</tr>
</tbody>
</table>

It was necessary to obtain a composite value of $[\langle r_o^2 \rangle / \langle M \rangle]^{1/2}$ for polyisoprene for the three isomeric components present, i.e. cis-1,4, trans-1,4
and 3,4 addition units. The composition was taken as that for sample G1 (table 4.2). No \( \langle \rho_0^2 \rangle / \rho_1^2 \) data was available for 3,4-polyisoprene and therefore as an approximation a value for poly(1-pentene) was used. The small amount of this component present meant an exact value was not essential. Substituting into equation (2.53) we get

\[
N_\text{PI} = 0.63 N_\text{PS}
\]  

(3.3)

where \( N_\text{PI} \) is the molecular weight of polyisoprene and \( N_\text{PS} \) the molecular weight of the polystyrene.

Values of \( \langle \rho_0^2 \rangle / \rho_1^2 \) for methylsubstituted styrene polymers are not that different from the polystyrene value (see table 3.15), and therefore the molecular weights were taken as obtained.

In cases where direct conversion via a calibration procedure could not be made values given as \( \tilde{M}_w^*, \tilde{M}_n^* \) and \( \tilde{M}_p^* \) represent polystyrene equivalents for the particular systems measured and are therefore not the true values for those polymers.

Values of \( \tilde{M}_w / \tilde{M}_n \) quoted throughout do not take into account peak broadening (section 2.4.4) and therefore are larger than the true values. For this reason the word 'uncorrected' is often added after values to emphasise this point.

3.5.2.4 Concentration calibration

In addition to the molecular weight determinations, g.p.c. was also used for obtaining the amounts of homopolymer (polystyrene and poly(\( \alpha \)-methylstyrene)) present in an SBR graft copolymer product. To carry out the procedure (see section 4.5) it was necessary to construct peak area versus concentration plots for SBR, polystyrene and poly(\( \alpha \)-methylstyrene). Sample M1 (metalated SBR and terminated with 2-propanol) was used as the
SBR sample in the concentration range 0.5 to 3.2 g\text{l}^{-1} (figure 3.7). The polystyrene calibration was obtained using a polystyrene standard (Polymer Laboratories, $M_p = 9,500$) in the concentration range 0.2 to 1.1 g\text{l}^{-1} (figure 3.8). The poly($\alpha$-methylstyrene) calibration was obtained using sample H9 ($M_p = 17,000$) in the concentration range 0.05 to 1.5 g\text{l}^{-1} (figure 3.9). Peak areas are expressed in arbitrary units.
FIGURE 3.8
Concentration calibration curve for polystyrene
(Polymer Laboratories polystyrene standard, $n_p = 9500$)
3.6 **HIGH SPEED MEMBRANE OSMOMETRY**

Direct measurement of number average molecular weight ($\bar{M}_n$) of graft and homo-polymers was made using high speed membrane osmometry. A Hewlett Packard osmometer (Model 502) was used as described in the instruction manual (211). Osmotic pressures ($\Pi$) were obtained for several different solution concentrations (2 - 12 gl$^{-1}$) for each polymer analysed. Measurements were carried out at room temperature using degassed toluene as solvent. The osmotic pressure and $\bar{M}_n$ are related according to the following virial expansion:

$$\frac{\Pi}{c} = \frac{RT}{\bar{M}_n} + Bc + Cc^2 + \ldots$$  \hspace{1cm} (3.4)

where $c$ is the solution concentration, $R$ is the gas constant, $T$ is the absolute temperature and $B$ and $C$ are the second and third virial coefficients. As $c$ approaches zero then

$$\left(\frac{\Pi}{c}\right)_{c \to 0} = \frac{RT}{\bar{M}_n}$$  \hspace{1cm} (3.5)

By plotting $\Pi/c$ against $c$, $\bar{M}_n$ can be determined from the intercept on the $\Pi/c$ axis, i.e. where $c = 0$. A typical plot is given in figure 3.10.

Because low molecular weight species are able to permeate through the membrane the method was only used for samples with $\bar{M}_n$ greater than 20,000.
Typical osmometry curve (sample 10) of \( \frac{n}{c} \) against \( c \) for the determination of \( n \).
3.7 OZONOLYSIS

To determine the molecular weight by g.p.c. of grafted polystyrene or poly(α-methylstyrene) in the SBR graft copolymers it was first necessary to isolate the grafted material by preferentially degrading the backbone polymer using ozonolysis techniques. Ozone was prepared by passing pure oxygen at low flow rates through a Towers Ozone Generator (GB-150). The apparatus operates on the principle of a silent high tension discharge (7.5 kV) across an annular space through which oxygen passes. The electrodes are continuously cooled by a weak electrolyte solution (0.2% wt. copper sulphate solution) surrounding the annular space. Ten such ozone units, each with its own effective annular space, are connected in series to an outlet manifold (figure 3.11). For a flow rate of 0.2 l min$^{-1}$ the ozone enriched oxygen contained 7.8% vol. ozone as determined iodimetrically (212). The ozonolysis procedure of Hackathorn and Brock (150) was followed. A small quantity of graft copolymer (0.1 g) was dissolved in chloroform (10 cm$^3$). The solution was then added to a small flask containing a magnetic follower and fitted with gas inlet and outlet as shown in figure 3.11. The flask was cooled to $-78^\circ$C using a methanol/solid carbon dioxide bath. Ozone enriched oxygen from the generator was passed through the solution for 30 minutes, during which time the solution turned a pale blue colour. The gas bubbler was then removed and a few crystals of triphenylphosphine were added to the solution. The colour quickly faded and the solution was then stirred at room temperature for 24 hours to remove most of the solvent. The remaining traces of solvent were removed by heating the flask in a vacuum oven at $60^\circ$C to constant weight (approximately 3 hours). The dried samples were analysed by g.p.c. as mentioned in section 3.5.
FIGURE 3.11
Ozonolysis apparatus

high tension terminals

7.5 kV transformer

oxygen supply

dreschel bottle to indicate gas flow

ozone unit with annular space

ozone supply

to fume cupboard

graft copolymer solution

methanol/solid carbon dioxide bath
3.8 NUCLEAR MAGNETIC RESONANCE

3.8.1 Proton NMR

Polymer composition was determined by $^1$H nuclear magnetic resonance (NMR) using a 90 MHz Perkin Elmer R-32 spectrometer. Polymer samples were prepared in carbon tetrachloride or deuterochloroform (3% w/v) and filtered before use. The spectra were calibrated with tetramethylsilane (TMS) equal to zero ppm magnetic field shift ($\delta = 0$). Integrated intensity values were obtained for $\delta$ over the range 10 to 0 ppm. All measurements were made at room temperature.

3.8.2 Carbon-13 NMR

$^{13}$C NMR spectroscopy was used in an attempt to identify the positions of the metalation sites in deuterated SBR (sample H5) by comparing the spectrum obtained with that of a non-deuterated sample (H3). A 20.1 MHz Bruker $^{13}$C NMR spectrometer was used. Polymer samples were prepared as above and TMS was again used as the internal standard. Measurements were taken at 40°C. $^1$H noise decoupled spectra were obtained over the range 150 to 0 ppm (TMS). Signal enhancement was achieved by scanning $2 \times 10^4$ times which was sufficient to eliminate nearly all background noise.
3.9 INFRA RED AND ULTRA VIOLET SPECTROSCOPY

Infra red spectra were obtained for carboxylated (sample #6) and untreated SBR. A Perkin Elmer 457 spectrometer was used. The samples were cast from chloroform on Melinex sheet. Trace solvent was removed by drying the samples under vacuum at 20°C for 48 hours. The thin films were removed from the Melinex sheet and their spectra run at room temperature using air as the reference. The spectral range covered was from 4,000 to 600 cm⁻¹.

Ultra violet spectra of the above polymers were obtained using a Unicam SP 8000 recording spectrometer. The samples were prepared in chloroform (1.0 g l⁻¹) and measurements made using 1 cm silica cells with pure chloroform used in the reference beam. Readings were taken at room temperature. The spectral range covered was from 190 to 400 nm.
SECTION C: PROPERTY EVALUATION

3.10 SAMPLE PREPARATION - MOULDED AND SOLVENT CAST

Two types of samples were prepared; solvent cast and moulded. Solvent cast films were prepared from cyclohexane or chloroform by dissolving a known amount of polymer in the solvent and then the solution (approx. 5% w/v) poured onto a smooth p.t.f.e. surface and allowed to stand at room temperature for several days until most of the solvent had evaporated. The remaining traces of solvent were removed by drying the films under vacuum for one week at room temperature. Films of 0.05 to 0.20 cm thickness were produced in this way.

Moulded samples were prepared by placing a small quantity of polymer (1.5 - 2.5 g) in a four piece compression mould and heating to 110 to 210°C at 13.8 MPa pressure for 0.5 to 4 hours. All samples were cooled under pressure. Approximate sample dimensions were 3.0 x 0.8 x (0.1 - 0.3) cm. The thickness was determined by the amount of charge used.
3.11 DIFFERENTIAL SCANNING CALORIMETRY

The glass transition temperatures \( T_g \) of homopolymers and graft copolymers were determined using a Du Pont 900 Differential Thermal Analyser equipped with a Differential Scanning Calorimetry accessory (catalogue ref. 900600). Samples (0.1 g) were scanned from \(-100\) to \(+200^\circ\text{C}\) at a heating rate of \(15^\circ\text{C min}^{-1}\). An empty sample pan was used as the reference. A plot of the temperature difference \( \Delta T \) between the sample and reference junction was plotted against the reference temperature. The temperature axis of the instrument was calibrated using mercury, benzophenone and benzoic acid which melt at \(-39\), \(48\) and \(122^\circ\text{C}\) respectively.

The glass transition was taken as the midpoint in the \( \Delta T \) step as shown by the idealised glass transition temperature in the schematic representation:

\[
\begin{align*}
\Delta T &= T_g \\
T_1 &< T_g < T_2
\end{align*}
\]

where

\[
T_g = 0.5 (T_1 + T_2) \quad (3.6)
\]
3.12 Dynamic Mechanical Thermal Analysis

The dynamic mechanical properties of solvent cast and moulded samples of SBR and polyisoprene graft copolymers over the temperature range -100 to 200°C were investigated using a Dynamic Mechanical Thermal Analyser (Polymer Laboratories). Direct readings of the log of the storage component of Young's modulus (E') and loss tangent (tan δ) against temperature were obtained at a constant frequency (1 Hz) and a heating rate of 5°C min⁻¹. The instrumental determination of E' and tan δ is as follows:

A rectangular bar sample clamped at both ends is oscillated in bending geometry by a central clamp. The clamp is driven by an electro-magnetic drive of the moving coil type. The force produced by the action of a sinusoidal current in the moving coil is resisted by the mass of the moving system, the rigidity of the sample and the rigidity of the instrument's spring plate. The equation of motion for such a system is given by:

\[ M\ddot{x} + kE^*x + sx = F_0 \exp(i\omega t) \]  \hspace{1cm} (3.7)

where \( M \) is the mass of the vibrating system
\( x \) is the linear displacement of the driven clamp
\( E^* \) is the complex rigidity modulus \((E' + iE'')\) of the specimen
\( F_0 \) is the maximum driving force
\( \omega \) is the angular frequency of the driving current
\( t \) is the time
\( S \) is a term for the rigidity of the spring plate
and
\( k \) is a geometrical factor, which for bending geometry is given as

\[ k = \frac{2bh^3}{l^3} \]  \hspace{1cm} (3.8)

where \( b \) is the width, \( h \) the thickness and \( l \) the length of each half of
the specimen between each rigid clamp and the central clamp.

By considering only peak force \( F_0 \) and peak amplitude the solution to the differential equation can be given in the form

\[
E' = \frac{1}{K} \left[ \frac{F_0}{X_0} \cos \beta - S + N \omega^2 \right] \quad (3.9)
\]

\[
E'' = \frac{1}{K} \frac{F_0}{X_0} \sin \beta \quad (3.10)
\]

where \( X_0 \) is the peak linear displacement and

\[
\beta = \tan^{-1} \left[ \frac{kE''}{kE' + S - M \omega^2} \right] \quad (3.11)
\]

\( X_0 \) is proportional to the peak value of the output voltage \( V \)

\[
X_0 = BV \quad (3.12)
\]

where \( B \) is a constant of the transducer system, and \( F_0 \) is proportional to the peak value of the driving current \( I \)

\[
F_0 = NI \quad (3.13)
\]

where \( N \) is a constant depending on the strength of the magnet and the properties of the coil. Combining equations (3.9) and (3.10) with equations (3.12) and (3.13) we get \( E' \) and \( E'' \) in terms of actual measurements

\[
E' = \frac{N}{KB} \left[ \frac{I}{V} \cos \beta \right] - \frac{S}{K} + \frac{M \omega^2}{K} \quad (3.14)
\]
\[ E'' = \frac{N}{kS} \left[ \frac{I}{V} \sin \beta \right] \quad (3.15) \]

and \[ \tan \delta = \frac{E''}{E'} \quad (3.16) \]

The instrument, by measuring a system under the following conditions, evaluates \( \left( \frac{N}{B} \right), S \) and \( M \),

1) no specimen, frequency setting 1 Hz, instrument in 'cal' mode, gives \( S \)
2) no specimen, frequency setting 30 Hz, instrument in 'cal' mode, Difference from 1) gives \( N \).
3) standard sample included and adjustment made in 'run' mode, until displayed value agrees with known modulus. This gives \( N/B \).

Values for \( k \) were determined from the dimensions of each sample and then dialled into the instrument. Satisfying all conditions in equations (3.14) and (3.15) values for \( E' \), \( E'' \) and subsequently \( \tan \delta \) (equation (3.16)) can then be given.
3.13 PHYSICAL PROPERTIES

3.13.1 Tensile Stress-Strain Behaviour

Half or full width moulded bars (approximate dimensions as given in section 3.10) and microdumbells (BS903 A2) cut from solvent cast films were tested on a JJ Tensile Tester at a crosshead speed of 4 cm min\(^{-1}\). Traces of load versus the increase in crosshead separation were obtained. Tensile strength was determined from the load at break and the cross-sectional area of the unstretched sample. Elongation at break was determined from the increase in distance between two points 2 cm apart and equidistant from the centre of the sample at the start of the test. All measurements were made at room temperature (20°C).

3.13.2 Compression Set

The standard test method for compression set under constant deflection (BS903 A6 (1969)) at 20°C states that a sample of 1.3 cm diameter and 0.633 cm thickness is compressed to 0.473 cm (i.e. 25% compression) for 72 hours using a device similar to that shown in figure 3.12. The sample is then removed from the apparatus and placed on a thermally non-conducting surface, e.g. wood, for thirty minutes before its final thickness is measured using a micrometer. The amount of material necessary for a test sample was prohibitive in the present work because only small quantities of polymer were prepared. It was therefore necessary to use non-standard test pieces, having a diameter 0.40 to 0.73 cm and thickness 0.19 to 0.27 cm. The small and varied sample sizes prevented a constant compression of 25% being applied to all samples, only a range of values was possible (15 to 65%) with the spacers available. All other conditions were as in the BS test using the rig shown (figure 3.12).
FIGURE 3.12
Device for compression set test under constant deflection

SIDE VIEW

END VIEW
Compression set was calculated as follows,

\[
\text{Compression set (\%)} = \frac{(t_o - t_r)}{(t_o - t_s)} \times 100
\]  \hspace{1cm} (3.17)

where \( t_o \) = original thickness of test piece
\( t_r \) = thickness of test piece after recovery
\( t_s \) = thickness of spacer.

3.13.3 Hardness

Sample hardness was measured using a Shore Durometer (type A2) on samples which were greater than 0.15 cm thick. Values in the Shore A range 30 to 100 can be regarded as being approximately equal to international rubber hardness degrees (IRHD).
CHAPTER 4

RESULTS AND DISCUSSION

SECTION A: SYNTHESIS AND CHARACTERISATION

4.1 POLYISOPRENE

The preparation of polyisoprene in hydrocarbon solvent was used as a model anionic system on which to evaluate g.p.c. and NMR analytical techniques and also obtain kinetic data.

The extent of polymerisation as a function of time for polyisoprene (sample H1) prepared in heptane using s-BuLi as initiator was followed by obtaining molecular weight values for samples withdrawn at various times during polymerisation. The $\bar{M}_n$ for each sample was determined by g.p.c., the polystyrene equivalent values were converted to polyisoprene values using equation (3.7), i.e. $M_{PI} = 0.63 M_{PS}$. A plot of $\bar{M}_n$ versus polymerisation time is given in figure 4.1. The shape of the curve can give us some insight into the initiation and propagation reactions.

4.1.1 Initiation and Propagation

The slow initiation reaction compared to that of propagation of some organolithium compounds with dienes in hydrocarbon solvents has been partially attributed to their existence as aggregates in these solvents (44). It is known (28) that s-BuLi exists as tetramers in cyclohexane and benzene. As mentioned in sections 2.1.1 and 2.1.2 the partial order kinetics are not directly related to the association number (28), an assumption which was based on the idea that only unassociated initiator was responsible for initiation. Initiation by both associated and unassociated initiator has been proposed (31). Roovers and Bywater (213)
FIGURE 4.1
Plot of $\bar{M}_n$ versus polymerisation time for the preparation of polyisoprene (sample H1) in n-heptane at 20°C using s-BuLi as initiator.

FIGURE 4.2
Conversion versus polymerisation time curves for the preparation of polyisoprene in cyclohexane at 50°C using s-BuLi (A) and n-BuLi (B) as initiators (214).
obtained data which clearly showed that the tetramers of s-BuLi were directly involved in the initiation reaction of isoprene in cyclohexane. The identification of initiating species from spectroscopic and kinetic data has been further complicated by the fact that the presence of the cross-associated species of s-BuLi and polyisoprenyllithium (28) may also play a role in the rate determining step. Where initiation is slower than propagation sigmoidal shaped monomer conversion versus time curves are often obtained. Typical curves (214) for the polymerisation of isoprene in cyclohexane at 50°C using n- and s-BuLi as initiators are given in figure 4.2. The initial part of the curve is a complex region in which both initiation and propagation reactions are taking place. When s-BuLi is used as initiator the initiation reaction is completed in a relatively short period. Since simultaneous initiation and propagation does not occur to any appreciable extent, the conversion curves only reflect the propagation process. When n-BuLi is used as the initiator a well defined 'induction period' is observed as the result of a very slow initiation reaction which affects the course of the reaction. Examination of the initiation reaction only of s-BuLi has shown that the conversion to polyisoprenyllithium does exhibit an induction period, however, the time scale involved is small and therefore would not be detected in figure 4.2. The reactivity of s-BuLi, in whatever form, towards isoprene is much greater than that of n-BuLi in the same hydrocarbon solvent.

In the present preparation (sample H1) a product yield of almost 100% was obtained. If we therefore regard figure 4.1 as a plot of monomer conversion against time, the reaction goes to completion ($\bar{M}_n = 26,100$) in approximately 8 hours. The curve passes through the origin as found with the polymerisation of isoprene in cyclohexane using s-BuLi as initiator (214), figure 4.2. There is no evidence of a slow initiation step in the present system where n-heptane is used as solvent. Support for this can
be gained by examining the g.p.c. curve of the final product (figure 4.3) and the g.p.c. results given in table 4.3. The polydispersity ($\overline{M}_w/\overline{M}_n$) value obtained was 1.16 (uncorrected). As mentioned in section 3.5.2.3 peak broadening tends to give larger than expected $\overline{M}_w/\overline{M}_n$ values. The determination of $\overline{M}_w/\overline{M}_n$ from g.p.c. results for a polystyrene standard (Waters, $\overline{M}_n = 33,000$, $\overline{M}_w/\overline{M}_n = 1.09$) gave a value of 1.13, therefore the polydispersity value obtained for the polyisoprene sample would suggest a very narrow molecular weight distribution polymer. If the rate of initiation had been significantly slower than the propagation rate a broader molecular weight distribution (larger $\overline{M}_w/\overline{M}_n$) would have been obtained. For this reason s-BuLi rather than n-BuLi was the preferred initiator used throughout.

4.1.2 Propagation kinetics

In a 'living' system molecular weight changes directly assess monomer consumption, i.e. monomer concentration ($C$) can be given as $C_0 \propto \overline{M}_n \infty$ and $C_t \propto (\overline{M}_n \infty - \overline{M}_n t)$ where $C_0$ and $C_t$ are the concentrations initially and at time $t$, respectively, and $\overline{M}_n t$ and $\overline{M}_n \infty$ are the number average molecular weights at time $t$ and at completion of reaction, respectively. To investigate the dependence of propagation rate on monomer concentration the data in figure 4.1 was used to construct a pseudo first-order plot of $\log [\overline{M}_n \infty/(\overline{M}_n \infty - \overline{M}_n t)]$ against time. A good first-order plot of monomer consumption over at least three half-life times was obtained (figure 4.4). A value of $6.6 \times 10^{-3} \text{ min}^{-1}$ was obtained for the pseudo first-order rate constant ($k_1$) which agrees quite well with the value obtained by Morton (42) of $9.0 \times 10^{-3} \text{ min}^{-1}$ for the n-BuLi initiated isoprene polymerisation in n-hexane at 29°C for the same initiator concentration of 4.3 M moles l$^{-1}$. For the proposed overall propagation rate expression, equation (2.21), values of $n = 0.17$ to 0.50 have been obtained (42, 47, 48, 62, 215, 216)
**FIGURE 4.1**
Gel permeation chromatogram of polyisoprene (sample HL)

**FIGURE 4.4**
First-order rate plot for the polymerisation of isoprene (sample HL)
for n- and s-BuLi initiated polymerisations of isoprene in hydrocarbon solvent. As mentioned in section 2.1.2, the kinetics of these reactions cannot be simply interpreted using expressions of the type given in equation (2.20) and therefore values for $k_2$ and ultimately $k_p$, have not been fully agreed upon because of the lack of a suitable mechanism to account for the kinetic results obtained. It was never the intention in this work to study kinetics per se and the limited data does not allow us to progress understanding in this area. However, it is useful to know that equation (2.10) describes the conversion in the present work.

4.1.3 Changes in Polydispersity with Degree of Polymerisation

For the ideal anionic polymerisation in which the conditions given in section 2.3.1 are satisfied, the resulting polymer will have a Poisson molecular weight distribution (118), equation (2.32), for which the approximation $\bar{x}_w/\bar{x}_n = 1 + (\bar{x}_n)^{-1}$ (equation (2.36)) holds at fairly large $\bar{x}_n$. As $\bar{x}_n$ increases then $(\bar{x}_w/\bar{x}_n) \to 1$. This is shown in figure 4.5 where polydispersity ($\bar{M}_w/\bar{M}_n$) is plotted against polymerisation time. Polydispersity decreases with polymerisation time because $\bar{x}_n$ (as illustrated by $\bar{M}_n$ in figure 4.1) increases as the reaction progresses. A test of the theoretical prediction, equation (2.36) is performed in figure 4.6 where polydispersity is plotted against $(\bar{x}_n)^{-1}$, where $\bar{x}_n$ values are determined for particular values of $\bar{M}_n$ given in figure 4.1. The observed increase in polydispersity with increasing $(\bar{x}_n)^{-1}$ is much greater than expected for an ideal system. Of the conditions mentioned in section 2.3.1, the one referring to the exclusion of all termination processes (a), is the least likely to be satisfied in the present preparation. Premature termination which will be more pronounced during the early stages of the synthesis may account for the rapid decrease in polydispersity as the reaction progresses. No corrections have been made for g.p.c. peak broadening and therefore the
FIGURE 4.5
Plot of polydispersity versus polymerisation time for polyisoprene (sample HI)

FIGURE 4.6
Plots of polydispersity versus $(\bar{x}_n)^{-1}$
Polydispersity values quoted are maximum values. Therefore to summarise these results we can say that the molecular weight distribution of polyisoprene broadens with decreasing degree of polymerisation as predicted, however, the effect is exaggerated when real rather than ideal conditions are employed and also by errors inherent in the measuring technique.

4.1.4 Microstructure

The microstructure of polyisoprene prepared in heptane was determined using $^1$H NMR as described in section 3.8.1. Four addition products are possible,

\[ \text{CH}_3 \quad \text{H} \]
\[ \text{C}=\text{C} \]
\[ \sim\text{CH}_2 \quad \text{CH}_2 \sim \]

I) $\sim$ cis-1,4 addition

\[ \text{C}=\text{C} \]
\[ \text{CH}_3 \quad \text{CH}_2 \sim \]

II) $\sim$ trans-1,4 addition

\[ \sim\text{CH}_2 \text{-CH}_2 \sim \]
\[ \text{C} \quad \text{CH}_3 \quad \text{CH}_2 \text{-CH}_2 \sim \]

III) $\sim$ 3,4 addition

\[ \sim\text{CH}_2 \text{-CH}_2 \sim \]
\[ \text{CH}_3 \quad \text{CH}_2 \]

IV) $\sim$ 1,2 addition

The peak assignments for each proton type are given in table 4.1, a typical spectrum obtained (sample H1) is given in figure 47. The absence of peaks at 4.95 $\delta$ and 1.05 $\delta$ suggests that no 1,2 units are present in the polymer. The relative amounts of cis- and trans-1,4 and 3,4 units
### Table 4.1

### 1H NMR Peak Assignments for Polyisoprene (217, 218)

<table>
<thead>
<tr>
<th>Peak ref.</th>
<th>Proton type (H)</th>
<th>Chemical shift $\delta$ (ppm from TMS)</th>
</tr>
</thead>
</table>
| A         | $-\text{CH}=\text{CH}_2$  
           | $\text{Me}$  
           | $-\text{CH}=\text{C}$- | 5.15 |
| B         | $-\text{CH}=\text{CH}_2$ | 4.95 |
| C         | $-\text{C}=	ext{CH}_2$ | 4.75 |
| D         | $-\text{CH}=	ext{C}=\text{C}$ (cis) | 2.07 |
| E         | $-\text{CH}=	ext{C}=\text{C}$ (trans) | 2.03 |
| F         | $\text{CH}_3\text{C}=\text{C}$ (cis) | 1.68 |
| G         | $\text{CH}_3\text{C}=\text{C}$ (trans) | 1.60 |
|           | $\text{CH}_3\text{C}=	ext{CH}_2$ | |
| H         | $-\text{CH}_2\text{C}=\text{C}$ | 1.40 |
| I         | $\text{CH}_3\text{C}=\text{C}$ | 1.05 |

### Table 4.2

### Polyisoprene Microstructure by NMR Analysis

<table>
<thead>
<tr>
<th>Sample ref. a</th>
<th>Structure (% wt.)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>cis-1,4 trans-1,4 1,2 3,4</td>
</tr>
<tr>
<td>H1</td>
<td>70.0 23.0 - 7.0</td>
</tr>
<tr>
<td>G1</td>
<td>70.6 22.2 - 7.2</td>
</tr>
</tbody>
</table>

a) for synthesis details see table 3.1.
Figure 1. NMR spectrum of polyisoprene (sample H1)
present were determined from the integrated peaks using the method of Chen (217). The relative amounts of structures I, II and III were obtained using the following simultaneous equations,

\[ [\text{III}] + 4[I] + 4[\text{II}] = \frac{\text{area (D + E)}}{T_1} \]  
\[ 3[I] = \frac{\text{area } F}{T_1} \]  
\[ 3[\text{II}] + 3[\text{III}] = \frac{\text{area } G}{T_1} \]

where \( T_1 \) is the total of areas \((D + E + F + G)\) and \([\ ]\) represent mole fractions. Areas are given in arbitrary units. A second determination of the relative molar amounts of 1,2 and 1,4 structures was carried out using the equations,

\[ [I + II] = \frac{\text{area } A}{T_2} \]  
\[ 2[\text{III}] = \frac{\text{area } C}{T_2} \]

where \( T_2 \) is the total of areas \((A + C)\).

Agreement between methods is good. The results for sample HI and the polyisoprene of sample GI are given in table 4.2. These results for samples prepared in heptane are very similar to other NMR results obtained for polyisoprene prepared in hydrocarbon solvents (61-63) as shown in table 2.1.
4.2 POLYISOPRENE-g-POLYSTYRENE

It was mentioned in section 2.2.3 that an n- or s-BuLi.TMEDA complex can metatate (lithiate) diene polymers, this reaction can be represented as follows:

\[ \text{RH} + \text{BuLi.TMEDA} \rightarrow \text{RLi.TMEDA} + \text{BuH} \] (4.6)

where R represents any group present in the polymer which has replaceable hydrogen. Spectroscopic studies by Hinoura et al. (108) and Clouet et al. (226) have shown that lithiation of polyisoprene occurs mainly at the methyl position with only a small amount of lithiation occurring in backbone positions \( \alpha \) to the double bond. Further discussion on metalation position is given in section 4.4.3 for the metalation of SBR.

The aim of the present work was to carry out grafting reactions on polyisoprene under various experimental conditions (table 3.1) using s-BuLi.TMEDA as metatating agent in hydrocarbon solvent and to analyse the products using g.p.c. techniques.

4.2.1 Interpretation of g.p.c. results

The g.p.c. results obtained for the polyisoprene backbone polymers prior to grafting are given in table 4.3. In several preparations the calculated molecular weights were less than the actual values (determined from the g.p.c. calibration relationship equation (3.3)), which suggests that some of the initiator was deactivated by impurities. If impurities are present during isoprene polymerisation the effect of premature termination will be to broaden the molecular distribution of the polymer. This may account for some of the larger than anticipated polydispersity values. The \( \bar{M}_n \) values for the samples prepared under argon blanket (G8 and G9), were in better agreement with the calculated values than the
### TABLE 4.3

Polyisoprene and Polyisoprene-g-polystyrene g.p.c. and yield results

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\bar{M}_n$ (x $10^{-3}$)</th>
<th>$\bar{M}_p$(theo) (x $10^{-3}$)</th>
<th>$\bar{M}_p$(obs) (x $10^{-3}$)</th>
<th>calc. $\bar{M}_p$ mol. wt. (x $10^{-3}$)</th>
<th>$\bar{M}_w$</th>
<th>$\bar{M}_n$ (x $10^{-3}$)</th>
<th>$\bar{M}_p$(theo) (x $10^{-3}$)</th>
<th>$\bar{M}_p$(obs) (x $10^{-3}$)</th>
<th>$\bar{M}_w$</th>
<th>Polystyrene yield (%)</th>
<th>$\Delta$</th>
<th>calc. graft mol. wt. (x $10^{-3}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H1</td>
<td>26.1</td>
<td>27.8</td>
<td>27.1</td>
<td>15.3</td>
<td>1.16</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>G1</td>
<td>40.4</td>
<td>48.2</td>
<td>46.0</td>
<td>20.4</td>
<td>1.43</td>
<td>46.7</td>
<td>70.5</td>
<td>56.0</td>
<td>1.48</td>
<td>85</td>
<td>2.7</td>
<td>6.1</td>
</tr>
<tr>
<td>G2</td>
<td>26.9</td>
<td>30.9</td>
<td>34.0</td>
<td>23.8</td>
<td>1.32</td>
<td>33.1</td>
<td>43.5</td>
<td>44.7</td>
<td>1.72</td>
<td>86</td>
<td>1.4</td>
<td>9.2</td>
</tr>
<tr>
<td>G3</td>
<td>6.2</td>
<td>6.7</td>
<td>6.3</td>
<td>8.5</td>
<td>1.17</td>
<td>6.9</td>
<td>8.5</td>
<td>8.8</td>
<td>1.51</td>
<td>60</td>
<td>0.4</td>
<td>3.2</td>
</tr>
<tr>
<td>G4</td>
<td>11.9</td>
<td>12.9</td>
<td>13.9</td>
<td>12.5</td>
<td>1.16</td>
<td>12.0</td>
<td>13.8</td>
<td>15.8</td>
<td>1.33</td>
<td>64</td>
<td>0.6</td>
<td>2.7</td>
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<tr>
<td>G5</td>
<td>34.1</td>
<td>37.9</td>
<td>42.2</td>
<td>10.9</td>
<td>1.23</td>
<td>43.5 (4.2)</td>
<td>50.0 (4.5)</td>
<td>50.4 (4.7)</td>
<td>1.32</td>
<td>95</td>
<td>4.8</td>
<td>4.4</td>
</tr>
<tr>
<td>G6f</td>
<td>36.5</td>
<td>39.7</td>
<td>39.7</td>
<td>31.3</td>
<td>1.19</td>
<td>36.1 (4.7)</td>
<td>39.5 (5.5)</td>
<td>41.0 (5.0)</td>
<td>1.29</td>
<td>43</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>G7</td>
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<td>74.1</td>
<td>72.4</td>
<td>28.6</td>
<td>1.35</td>
<td>-</td>
<td>-</td>
<td>72.5 (5.2)</td>
<td>-</td>
<td>93</td>
<td>-</td>
<td>-</td>
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<td>130.0</td>
<td>132.3</td>
<td>90.9</td>
<td>1.53</td>
<td>149.2</td>
<td>211.1</td>
<td>201.6</td>
<td>2.00</td>
<td>74</td>
<td>9.9</td>
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</tr>
<tr>
<td>G9</td>
<td>45.4</td>
<td>50.0</td>
<td>44.1</td>
<td>50.0</td>
<td>1.21</td>
<td>45.4 (1.8)</td>
<td>50.0 (1.9)</td>
<td>44.1 (1.8)</td>
<td>1.21</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Values in ( ) are for styrene homopolymers and are uncorrected.

a) to f) See page 123.
a) For synthesis details see table 3.1.

b) Calculated polyisoprene molecular weight = $[s$-BuLi]$^{-1}$ where $[s$-BuLi] is the isoprene initiator concentration (moles/g isoprene).

c) Polystyrene yield ($\%$) = \frac{\text{weight of styrene polymerised (g)}}{\text{initial weight of monomer}} \times 100, (based on a 100% conversion of isoprene to polymer).

d) Average number of graft sites per chain ($A$) = $\bar{n}_{[s$-BuLi]$_m$}, where $[s$-BuLi]$_m$ is the metalation initiator concentration (moles/g isoprene).

e) Calculated graft molecular weight = $Y \bar{M}$ ($\bar{M}$$_{(1-F)}$ - $\bar{M}$$_n$) where $Y$ is the (fractional) yield of polystyrene and $F$ is the fraction of styrene in the total monomer feed.

f) For explanation of results see section 4.2.5.
samples prepared under nitrogen blanket in the absence of trace indicators (see section 4.2.4).

From the limited amount of calibration data available and for the purposes of comparison with the polyisoprene backbone polymers, the molecular weight parameters for the graft copolymers are expressed as linear polymer polyisoprene equivalents, determined from the polystyrene calibration (figure 3.5) values using equation (3.3). These graft copolymer approximate molecular parameters (denoted **) are given, together with the other g.p.c. results for the backbone polymers, in table 4.3. From a calculation of the graft polystyrene molecular weight and allowing for incomplete conversion the results show that $R_n^{**}$ values from g.p.c. are always a low estimate of the graft copolymer molecular weight.

As mentioned in section 2.3.2, random anionic grafting onto a monodisperse polymer increases its polydispersity by an amount determined by the number of grafts per molecule and the graft molecular weight (figure 3.2). Although the results in table 4.3 show an increase in the polydispersity of the polymer on grafting, precise comparisons between theory and experiment are not possible because,

a) all polydispersity values are uncorrected for machine broadening,
b) the backbone polymers are not monodisperse and their polydispersity values vary,
c) polydispersity is experimentally determined from $R_n^{**}$ and is therefore an approximate value.

The g.p.c. traces for samples G2, G3 and G5 before and after grafting are shown in figures 4.8 to 4.10. It can be clearly seen that the molecular weight increases on grafting as shown by the decrease in % TPE path length values. The broadening of the g.p.c. traces on grafting is also a clear indication of the increase in the molecular weight distributions of the polymers.
Differential Refractive Index

Graft Copolymer

Counts
Differential Refractive Index

Polyisoprene-g-Polyethylene (Sample G)

Polyisoprene chromographs of polyisoprene and

Figure 4.9
Light scattering measurements by Hadjichristidis and Hoovers (219) on anionically prepared polyisoprene-g-polystyrene copolymers showed an increase in $<s^2>$, the real mean-square radius of gyration, on going from ungrafted to grafted polyisoprene with THF as the solvent. If we assume $[<s^2>]^\frac{1}{2}$ values are proportional to hydrodynamic volume (see section 2.4.3) the molecular weight of the polymer, determined by g.p.c., should increase on grafting. For a branched homopolymer of polyisoprene the g.p.c. molecular weight values obtained will be larger than the true value because we are using a calibration for a linear polymer and it is known (220) that branched polymers have smaller hydrodynamic volumes than their linear counterparts of the same molecular weight. This can be seen in the explanatory diagram, figure 4.11. The calibration curve for polyisoprene lies above the hypothetical curve for a branched polyisoprene polymer of constant branch (graft) length and density. As we are actually looking at copolymers of isoprene and styrene we must consider the effect of replacing isoprene with styrene in the grafts. For linear polymers polystyrene has a larger hydrodynamic volume than polyisoprene for the same molecular weight and therefore has a g.p.c. calibration curve above that of polyisoprene as shown in the diagram. Block copolymers of styrene and isoprene will have calibration curves between those of the individual homopolymers with their positions determined by their relative abundance as given by Dawkins (135), see section 2.4.3. In the present work it is not possible to construct a single calibration curve for the graft copolymers in a similar way to that mentioned for block copolymers because the variables, molecular weight, copolymer composition and graft density each affect the hydrodynamic volume. However, for a graft copolymer of fixed composition and structure a hypothetical calibration curve can be constructed, under such conditions two possible calibrations (A and B) for polyisoprene-g-polystyrene are given in figure 4.11.

For the samples given in table 4.3 polydispersity increases of up to
FIGURE 4.11

Hypothetical g.p.c. calibration curves for polystyrene, polyisoprene (linear and branched) and polyisoprene-g-polystyrene (A and B)

POLYSTYRENE

POLYISOPRENE

BRANCHED POLYISOPRENE
WITH CONSTANT BRANCH LENGTH AND BRANCH DENSITY

LOG M

RETENTION VOLUME ($V_R$)
0.5 are obtained. From the calculated average number of graft sites per chain (A) and graft molecular weights for these polymers, the maximum theoretical increase in polydispersity would be approximately 0.03 (figure ??). It is unlikely that the large differences in polydispersity increase between experiment and theory can be fully accounted for by a), b) and c) given above, and therefore other potential sources of actual or observed changes in polydispersity must be considered. One possibility arises as the result of the graft site distribution. For example, a polymer with \( A = 10 \) will have a probability distribution for 0 to 20 graft sites as shown in figure 2.1. It can be seen that although the average number of sites is 10 the actual probability of finding a chain with this number of sites is only 0.12. The consequences of having a polymer with such a range of sites is important in the present work where the amount of styrene incorporated in each polymer chain will also vary. As mentioned earlier g.p.c. separates polymers according to hydrodynamic volume and we have also discussed the effect grafting and the inclusion of styrene into the polymer have on hydrodynamic volume, however, let us now consider a single graft copolymer sample of fixed styrene content. The effect of a distribution of graft sites means that there will be a distribution of styrene contents, i.e. a chain with a large number of grafts will have a high styrene content, similarly for a small number of sites the styrene content will only be a very small fraction of the total polymer. The decrease in styrene with increasing retention (elution) volume will artificially broaden the g.p.c. molecular weight distribution curve on the high molecular weight side. This effect will be more noticeable for large values of \( A \), e.g. sample G8 where \( A \approx 10 \).

Up to now all the reasons for the larger than anticipated polydispersity increases have been attributed to an inadequacy in measuring, however, the increases may be due to real effects which occur as the
result of other chemical reactions taking place at the same time as the metalation and styrene polymerisation reactions. Side reactions have been proposed by several workers. Tate and coworkers (110) observed a decrease in solution viscosity for polybutadiene and polyisoprene in heptane at 50°C after metalating the polymers for several hours with n-BuLi.TMEDA. They attributed the decreases to chain scission via the vinyl and isoprenyl sites in polybutadiene and polyisoprene, respectively. Chain scission reactions would produce a noticeable 'tail' on the low molecular weight side of the g.p.c. distribution. The metalation of polybutadiene with n-BuLi.TMEDA in n-hexane has been studied spectroscopically by Hay et al. (221). The characteristic yellow metalation colour ($\lambda_{\text{max}} = 315$ nm) rapidly changed to a deep red colour ($\lambda_{\text{max}} = 365$ nm) on heating the solution to 70 to 80°C, or more slowly on standing at room temperature for several weeks. They suggested the colour change was due to an increase in conjugation of the carbanionic species as the result of a proton transfer reaction between the active polymer and an unsaturated polydiene unit. This newly formed species was inactive towards further butadiene polymerisation. If this also applies to styrene polymerisation it will effectively mean grafting will only occur at certain sites and that the graft molecular weights will be larger than expected. Szwarc et al. (222) proposed a mechanism for the slow spectral changes which occur with solutions of 'living' polystyrene on standing for long periods. For polystyrylsodium in THF or benzene,

\[ \text{--CH}_2\text{-CHNa} \rightarrow \text{--CH}=\text{CH} + \text{NaH} \] (4.7)

\[ \text{--CH}_2\text{-CHNa + CH}=\text{CH}-\text{CH}=\text{CH} \rightarrow \text{--CH}_2\text{-CHNa + CH}=\text{CH}-\text{CH}=\text{CH} \] (4.8)

The resulting carbanion is incapable of further polymerisation. The
similarity between this mechanism and the one proposed by Hay above, suggests that proton transfer reactions may occur between living polystyrene (Na or Li as counterion) and metalated sites and/or unsaturated regions of backbone polymer. Transfer reactions of this type will broaden the molecular weight distribution. Nentwig and Sinn (223) have reported bimodal molecular weight distributions for polybutadiene when the living polymer solution was heated to 80°C. A mechanism to account for the two products was suggested.

\[ \text{CH}_2=\text{CH}-\text{CH}-\text{CH}_2\text{Li} + \text{LiCH}_2=\text{CH}-\text{CH} = \text{CH}_2 \rightarrow \]
\[ \text{CH}_2=\text{CH}-\text{CH}=\text{CHLi} - \text{CH}_2=\text{CH} = \text{CH}_2 \]  

(4.9)

Carbon dioxide has been shown (60) to lead to chain coupling involving polystyryllithium (see section 2.1.3). More recently it has been claimed (207, 224) that oxygen can cause the coupling of organolithium compounds and that the reaction is enhanced by the presence of THEDA. Coupling reactions involving metalated and grafted polymers would not be restricted to the joining of just two molecules and could, in the extreme case, produce a completely crosslinked gel. It has been reported by Tate et al. (110) that the exposure of metalated polybutadiene to the atmosphere gives immediate and complete gelation. Less extensive crosslinking reactions of this kind would produce a high molecular weight 'tail' in the g.p.c. trace.

In the present work the g.p.c. traces for polyisoprene and metalated polyisoprene were in most cases identical. We can therefore eliminate the possibility of chain scission occurring during metalation for the experimental conditions used.

The g.p.c. traces (figures 4.8 - 4.10) indicate peak broadening on the high molecular weight side on grafting, as expected, however, the absence of any changes on the low molecular weight side of the curves suggests that
transfer reactions of the type mentioned above do not occur to any measurable extent. Figure 4.10 also shows a second polymeric species of lower molecular weight is present as a small fraction of the total product. This is low molecular weight ($\bar{M}_n = 4,200$) polystyrene with a narrow molecular weight distribution, $\bar{M}_w/\bar{M}_n = 1.14$ (uncorrected), which formed as the result of an inefficient metatation reaction (see section 4.2.2). If we assume the molecular weight of the homopolymer is the same as that of the grafts (see section 4.10.2) we can compare the actual graft molecular weight with the calculated value. Allowing for a 95% conversion, the calculated value given in table 4.3 for sample G5 is in good agreement with the $\bar{M}_n$ and $M_p$ values. From this and the low polydispersity value it can be inferred that the formation of 'inactive' anionic species either on the backbone polymer or on the polystyrene (graft and homopolymer) does not occur. It is therefore possible that the broadening of the graft copolymer molecular weight distribution curves is the result of partial crosslinking reactions caused by impurities such as oxygen and carbon dioxide being present.

4.2.2 Further Comments on g.p.c.

The theoretical peak molecular weight, $M_p(\text{theo})$, obtained for a log-normal distribution as mentioned in section 2.4.2, i.e. using the equation $M_p(\text{theo}) = (\bar{M}_n \cdot \bar{M}_w)^{1/2}$, and the observed peak molecular weight, $M_p(\text{obs})$, obtained from the peak maximum of the g.p.c. trace, are given in table 4.3 together with their ** counterparts, for the purposes of comparison. $M_p(\text{theo})$ and $M_p(\text{obs})$ are in good agreement for nearly all samples and therefore the normalised molecular weight curves for these polymers approximate to log-normal distributions.

A comparison can also be made between the peak molecular weights and the $\bar{M}_n$ values for each sample. These are in reasonable agreement only for samples with low polydispersity values and therefore the relationship $M_p \approx \bar{M}_n$ as suggested by equation (2.43) applies only for narrow molecular
weight distribution fractions. For a log-normal distribution $M_p$ is expressed by (124)

$$\tilde{M}_n = M_p e^{-\beta^2/4}$$  \hspace{1cm} (4.10)

where $\beta$ is a parameter related to the breadth of the molecular weight distribution and $a$ is the Mark-Houwink exponent, equation (2.50). Without values of $\beta$ and $a$, $\tilde{M}_n$ cannot be determined from values of $M_p$ for broad log-normal distributions.

4.2.3 Experimental Conditions

For the preparation of the polyisoprene backbone polymers listed in table 4.3 and in the absence of premature termination, the various experimental conditions (see table 3.1) were found adequate for complete conversion of monomer to polymer prior to metalation, as shown by the single peak g.p.c. traces (single $\tilde{M}_n$ and $M_p$ values) for the polyisoprene products. Similarly, the absence of any detectable homopolymer in the final product g.p.c. traces of the graft copolymers prepared in heptane suggests an efficient metalation process for the range of conditions employed.

Two attempts (G5, G9) at grafting in cyclohexane using s-BuLi.TMEDA as metalating agent were carried out. In the G9 preparation the polyisoprene did not appear to increase in molecular weight on styrene polymerisation as shown by the g.p.c. results in table 4.3. The formation of a large homopolymer peak in the final product g.p.c. trace suggests that metalation of the backbone polymer has not occurred, and that all the polystyrene appears as homopolymer. In the other preparation (sample G5) metalation was performed at $50^\circ C$ and for two hours instead of one as in the previous preparation. A definite shift and broadening of the g.p.c. polyisoprene peak (figure 4.10) occurred on styrene polymerisation which
suggests that grafting has occurred. However, the presence of a small amount of low molecular weight homopolymer ($M_n = 4,200$) means that the grafting reaction is not 100% efficient. (Grafting efficiency is discussed in more detail in the JBR sections.) In view of the high grafting efficiencies (as defined in equation (4.17)) obtained by Falk and coworkers (15) for the same polymer system and experimental conditions as sample G5, the large amount of metalating agent used in this one particular case may be the reason for inefficient grafting. Although the absence of homopolymer in the n-heptane preparations suggests that this is a better solvent than cyclohexane in which to carry out the grafting reactions, n-heptane is not recognised (127) as a good solvent for polystyrene. The apparent lack of precipitate in the present preparations (G1-G4, G6 and G8) can probably be related to the fact that the polystyrene in the form of graft material and at the particular levels used is soluble, however, because of the possibility of precipitate formation at higher polystyrene (molecular weight) levels it was not used further.

The need for TMEDA to be present for metalation to occur is highlighted by the g.p.c. results obtained for sample G7 (table 4.3) in which no TMEDA was used. The apparent lack of a change in $M_p(\text{obs})$ for the isoprene polymer on styrene polymerisation and the presence of a large homopolymer peak in the g.p.c. trace strongly suggests that metalation of a diene polymer with s-BuLi will only occur in the presence of TMEDA, as confirmed by other workers (108, 225). The large amounts of TMEDA used in excess of the 1:1 TMEDA:s-BuLi molar ratio helped in reducing the solution viscosity and therefore aided in the stirring of the solutions (for further discussion see section 4.6.2).

The styrene polymerisation yields based on complete conversion of isoprene to polymer cover a range of 43 to 95% (table 4.3). High yields are obtained for the reactions carried out at elevated temperatures ($50^\circ$C) and for long polymerisation times ($>10$ hours).
4.2.4 Experimental Technique

As mentioned in section 3.2.1, several modifications to the basic polymerisation procedure were adopted to ensure complete polymerisation of isoprene prior to metalation and grafting. The addition of trace amounts of s-BuLi and styrene, as a colour indicator of solvent purity prior to the addition of isoprene and the main quantity of initiator (samples G3 and G4), did not affect the course of the polymerisation, as evidenced by the single peak, narrow molecular weight distribution g.p.c. traces obtained for the polyisoprene samples ($\bar{M}_n$ and $\bar{M}_w/\bar{M}_n$ values are given in table 4.3). The absence of other peaks also suggests that the trace amounts of poly­styrene formed are not detectable at the g.p.c. concentrations used. In general only small amounts of s-BuLi were required to produce colour, indicating that purity conditions could be adequately achieved by the methods used.

The preparations in which a second quantity of initiator was added at the end of the designated isoprene polymerisation period as a check for premature termination (samples G1 and G2) gave identical single peak g.p.c. traces for samples taken before and 4 hours after the second initiator addition. Polymerisation of isoprene was therefore assumed complete prior to the addition of the second quantity of initiator. Incomplete isoprene polymerisation has been observed occasionally and its effects on the metalation and grafting reactions are discussed in section 4.2.5.

Styrene and TMEDA added at the end of the isoprene polymerisation period as a colour indicator for a living system (samples G2, G3 and G4) did not show any signs, in the g.p.c. traces, of affecting the polymerisation, metalation or grafting reactions. The cross-over reaction of polyisoprenyllithium to polystyryllithium appeared only to take place in the presence of TMEDA. It is known (74) that ethers accelerate this cross-over reaction and we have found that TMEDA behaves similarly.
4.2.5 Incomplete Isoprene Polymerisation

The importance of ensuring isoprene is completely polymerised prior to metation is demonstrated by the g.p.c. results (table 4.3) and traces (figure 4.12) obtained for sample G6. Trace (A) was taken prior to metation, (B) at the end of the metation period and (C) at the end of the styrene polymerisation period. The presence of a second polyisoprene peak in trace (B) was caused by the metation quantity of initiator polymerising isoprene still present after the designated polymerisation period. The addition of styrene (trace (C)) causes a shift in peak position in this second peak due to block copolymer formation. The original polyisoprene g.p.c. peak does not increase in molecular weight throughout the metation and styrene polymerisation periods. The presence of isoprene during the metation period, therefore, prevents backbone metation and subsequently styrene grafting from occurring.
FIGURE 4.12

Gel permeation chromatograms taken prior to metatation (A), at the end of metatation (B) and at the end of the styrene polymerisation period (C) for sample G6.
4.3 POLYISOPRENE-\textit{g}-POLY(\alpha-METHYLSTYRENE)

It was mentioned in Chapter One that \(\alpha\)-methylstyrene used as the A block in ABA thermoplastic elastomers produces materials with superior use temperatures over those of conventional styrene-butadiene-styrene block copolymers (20, 21) and therefore the potential of \(\alpha\)-methylstyrene as a grafting monomer in anionic systems cannot be overlooked. Although the grafting of polyisoprene with \(\alpha\)-methylstyrene using \(s\text{-BuLi,TMEDA}\) as the metalating agent has been reported elsewhere (15) two preparations were carried out in the present work for the purposes of familiarisation with the techniques involved and the determination of the effectiveness of the different experimental conditions used prior to the preparation of SBR-\textit{g}-poly(\(\alpha\)-methylstyrene) copolymers (section 4.7).

As mentioned in section 3.2.2.2 polymerisation of \(\alpha\)-methylstyrene must be carried out at low temperatures because of the low ceiling temperature \((T_c)\) of the polymer, i.e. the temperature at which polymerisation and depolymerisation rates are equal. Although \(T_c\) is a function of the monomer concentration (227), absolute values of \(T_c\) for \(\alpha\)-methylstyrene have been obtained in the range 51 to 61°C (204, 206, 228) for polar and non-polar solvents. Measurable amounts of monomer (in equilibrium) have been found at temperatures down to -40°C (206), and therefore even at temperatures well below \(T_c\) it is still possible to have incomplete polymerisation. As shown in table 3.2 the polymerisation of \(\alpha\)-methylstyrene was carried out at -20°C for sample S1 and -78°C for sample S2. The yields given in table 4.4 show that a much higher yield is achieved in a shorter period when \(\alpha\)-methylstyrene polymerisation is carried out at -78°C. The various molecular weight parameters for the two preparations are given in table 4.4. As with the grafting of polyisoprene with styrene there is better agreement between \(M_n\) and \(M_p\) values at lower polydispersity values. The polyisoprene calculated molecular weights are less than the g.p.c. \(M_n\)
### TABLE 4.4

Polyisoprene and Polyisoprene-g-poly(α-methylstyrene) g.p.c. and yield results

<table>
<thead>
<tr>
<th>Sample ref.</th>
<th>Polyisoprene</th>
<th>Polyisoprene-g-poly(α-methylstyrene)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$M_n$</td>
<td>$M_p$ (theo)</td>
</tr>
<tr>
<td>31</td>
<td>31.8</td>
<td>34.5</td>
</tr>
<tr>
<td>32</td>
<td>43.7</td>
<td>49.6</td>
</tr>
</tbody>
</table>

Values in ( ) are for α-methylstyrene homopolymer and are given as styrene equivalents (see section 3.5.2).

a) For synthesis details see table 3.2.

b)-e) as for table 4.3 only replacing styrene with α-methylstyrene.
values obtained which suggests that some of the initiator has been deactivated by impurities. The g.p.c. traces for the polyisoprene samples taken at the end of the second initiator period (figures 4.13 and 4.14) show only single peaks, indicating isoprene polymerisation was complete prior to the addition of the second initiator amounts. The molecular weight parameters for the grafted polymers are, like the polyisoprene-$g$-polystyrene samples, expressed as polyisoprene equivalents. The calculated increases in polyisoprene molecular weight on grafting, determined from the product of the calculated number of graft sites and graft molecular weight for the particular yields obtained, are in poor agreement with the g.p.c. estimates. However, the g.p.c. traces of the final products, compared to those of the polyisoprene backbone polymers, (figures 4.13 and 4.14) do show peak broadening and a shift to higher molecular weight, which strongly suggests that grafting has occurred. The presence of a small homopolymer peak in the g.p.c. trace of S2 would indicate that not all the initiator present during the metalation period had reacted with the polyisoprene and which may be related to shorter metalation time employed. The efficiency of the metalation reaction is considered in more detail in the following SBR sections. Comparing the calculated graft molecular weight with that for the homopolymer (table 4.4) and assuming that they should be the same, the differences observed suggest that considerable amounts of initiator have been terminated. This is probably a consequence of adding THF after the metalation quantities of initiator have been added.

In conclusion it can be said that although g.p.c. methods can be used for the determination of the various molecular weight characteristics of polyisoprene and other homopolymers there are limitations to the accuracy of the technique when determining the molecular weights and polydispersity values of graft copolymers such as polyisoprene-$g$-polystyrene and polyisoprene-$g$-poly($\alpha$-methylstyrene) and therefore only approximate values
can be given. G.p.c. can, however, be used for determining the extent of metalation and whether grafting has actually occurred or not and, as will be shown in section 4.10.2 the presence of homopolymer can be used as a means for determining the graft molecular weight and polydispersity.
4.4 METALATION OF SBR

To eliminate problems such as premature termination and incomplete polymerisation found when preparing backbone polymers in situ (section 4.2) and to ensure a backbone polymer with a uniform molecular weight could be used throughout, a preformed commercial polymer was chosen as the substrate on which to carry out grafting reactions. SBR (Solprene 1204) was chosen because it can be obtained in a pure state and with no additives present. All metalation and grafting reactions of SBR were performed using argon blanket methods (section 3.2.2) because of the ease with which these procedures can be used when several solvents or low temperature polymerisations are involved.

In order to evaluate the effects of metalation on SBR it was first necessary to obtain information on the composition, structure and molecular weight characteristics of the unmetalated SBR.

4.4.1 Characterisation of Unmetalated SBR

The commercial SBR (Solprene 1204) used in the present work is described (14) as a solution polymerised random copolymer of styrene and butadiene. As mentioned in section 2.1.5, copolymerisation of styrene and butadiene in hydrocarbon solvent, because of the differences in the rate constants, produces predominantly block material. Although no specific details are given, randomisation of the monomer units in the preparation of Solprene 1204 is probably achieved by the addition of a suitable polar material to the polymerisation mixture. Randomisation can also be achieved by the incremental addition of butadiene to the reaction mixture, however, in view of the large amounts of 1,2-(vinyl) component present (table 4.8) the use of a polar material seems more likely (see section 2.1.4).
G.p.c.

A typical g.p.c. trace for the SBR is given in figure 4.15. The bimodal trace obtained was resolved into two peaks as shown and g.p.c. molecular weight characteristics obtained for the separate components and combined trace (table 4.5). All values are expressed in polystyrene equivalents and therefore are used only for comparison purposes. To obtain true values from g.p.c., molecular weight standards of a random styrene-butadiene copolymer of the same composition would be required. The small high molecular weight peak corresponds to a certain proportion of copolymer existing as star block copolymer, i.e. where several linear polymers of molecular dimensions given by the large g.p.c. peak are joined together to produce a polymer with a higher molecular weight. The $M_n^*$ and $M_p^{(obs)}$ values suggest a four arm polymer. We are, however, making a direct comparison between a linear and branched polymer and as mentioned in section 4.2.1 this introduces errors. Nevertheless, the high molecular weight component has been confirmed (230) as four arm star block material. No information is available on the type of linking agent used but, as mentioned in section 2.2.2, silicon tetrachloride is known to be a very efficient linking agent for polybutadienyllithium. It would then only involve a simple process of adding a small amount of butadiene at the end of the copolymerisation period and prior to the addition of the linking agent to ensure all the chains had a butadiene end group necessary for efficient linking. The star polymer may be made in the presence of unlinked material or prepared separately and then added to the linear polymer. Whatever the procedure used there appears to be no partially linked, i.e. two or three arm material, present, as evidenced by the sharpness of the g.p.c. trace in this region. From peak area measurements the star block copolymer is present as approximately 26% wt. of the total polymer. Branched polymers are usually added to unvulcanised rubbers because they improve processability and reduce cold flow.
FIGURE 4.15
Gel permeation chromatogram of unmetalated SBR (Solprene 1204)
**TABLE 4.5**

G.p.c. Results for SBR

<table>
<thead>
<tr>
<th>SBR a</th>
<th>$\bar{M}_n^*$ (x 10^{-3})</th>
<th>$\bar{M}_{p(\text{obs})}^*$ (x 10^{-3})</th>
<th>$\bar{M}_w^<em>/\bar{M}_n^</em>$</th>
</tr>
</thead>
<tbody>
<tr>
<td>complete sample b</td>
<td>250.0</td>
<td>-</td>
<td>1.83</td>
</tr>
<tr>
<td>resolved large peak</td>
<td>207.0</td>
<td>233.0</td>
<td>1.27</td>
</tr>
<tr>
<td>resolved small peak</td>
<td>885.0</td>
<td>910.0</td>
<td>1.30</td>
</tr>
</tbody>
</table>

a) figure 4.15

b) Literature values (229) for Solprene 1204, $\bar{M}_n = 151,000$

$\bar{M}_w/\bar{M}_n = 1.9$.

**TABLE 4.6**

G.p.c. Results for Metalated SBR Samples Terminated with 2-propanol

<table>
<thead>
<tr>
<th>Sample reference a</th>
<th>$\bar{M}_n^*$ (x 10^{-3})</th>
<th>$\bar{M}_{p(\text{obs})}^*$ (x 10^{-3})</th>
<th>$\bar{M}_w^<em>/\bar{M}_n^</em>$</th>
</tr>
</thead>
<tbody>
<tr>
<td>M1</td>
<td>217.0</td>
<td>240.0</td>
<td>1.33</td>
</tr>
<tr>
<td>M2</td>
<td>214.0</td>
<td>230.0</td>
<td>1.31</td>
</tr>
<tr>
<td>M3</td>
<td>159.0</td>
<td>200.0</td>
<td>1.50</td>
</tr>
<tr>
<td>M4</td>
<td>79.8</td>
<td>180.0</td>
<td>2.79</td>
</tr>
</tbody>
</table>

a) for synthesis details see table 3.14.
To obtain information on the composition and microstructure, unmethylated SBR was analysed by $^1$H NMR. The spectrum obtained is given in figure 4.16. Peak assignments are listed in table 4.7. Resolution was not sufficient to distinguish cis- and trans-1,4 addition components. Using the method suggested by Senn (231) for the determination of the relative amounts of styrene and butadiene 1,2 and 1,4 addition units present in a styrene-butadiene copolymer, the following expressions were derived,

$$\text{[styrene]} = \frac{(\text{area J/5})}{T_3}$$  \hspace{1cm} (4.11)

$$\text{[1,2-butadiene]} = \frac{(\text{area L/2})}{T_3}$$  \hspace{1cm} (4.12)

$$\text{[1,4-butadiene]} = \frac{(\text{area K/3}) - (\text{area L/4})}{T_3}$$ \hspace{1cm} (4.13)

where [ ] represent mole fractions and areas J, K and L are the integrated areas for the respective peaks given in table 4.7, arbitrary units are used. $T_3$ is the total area of the three components, i.e.

$$T_3 = \frac{\text{area J}}{5} + \frac{\text{area K}}{2} + \frac{\text{area L}}{4}$$ \hspace{1cm} (4.14)

Converting the mole fractions to weight percentage values, the results are given in table 4.8. Comparing these with the literature values (14) there appears to be good agreement. As mentioned in section 2.1.4, the polymerisation of butadiene in hydrocarbon solvent produces predominantly cis-1,4 addition product and therefore the deviation in the present system, as mentioned above, is undoubtedly due to the presence of a small amount of a polar material. Using a polar material as the actual
### TABLE 4.7

**$^1$H NMR Peak Assignments for Styrene-Butadiene Copolymers (218, 231)**

<table>
<thead>
<tr>
<th>Peak ref.</th>
<th>Proton type ($H$)</th>
<th>Chemical shift, $\delta$ (ppm from TMS)</th>
</tr>
</thead>
<tbody>
<tr>
<td>J</td>
<td>$H$</td>
<td>7.10</td>
</tr>
<tr>
<td>K</td>
<td>$-CH=CH-$</td>
<td>5.25</td>
</tr>
<tr>
<td>L</td>
<td>$-CH=CH_2$</td>
<td>4.95</td>
</tr>
<tr>
<td>M</td>
<td>$-CH_2-C=C-$</td>
<td>2.10</td>
</tr>
<tr>
<td>N</td>
<td>$-CH_2-C-C$</td>
<td>1.40</td>
</tr>
</tbody>
</table>

### TABLE 4.8

**SBR Microstructure by NMR Analysis**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Structural units (% wt.)</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Styrene</td>
<td>butadiene (1,2-)</td>
<td>butadiene (1,4-)</td>
</tr>
<tr>
<td>SBR</td>
<td>25.1</td>
<td>24.7</td>
<td>50.2</td>
</tr>
<tr>
<td></td>
<td>(26)</td>
<td>(22)</td>
<td>(52)$^a$</td>
</tr>
<tr>
<td>metalated SBR</td>
<td>24.3</td>
<td>25.7</td>
<td>49.0</td>
</tr>
<tr>
<td>(N3)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Values in ( ) determined by infrared spectroscopy (14).

a) 20% cis, 32% trans.
solvent or cosolvent would, however, produce a larger amount of 1,2-adduct than that actually obtained.

4.4.2 Characterisation of Metalated SBR

To investigate the effects of s-BuLi.TMEDA on SBR, three groups of experiments were carried out in which the metalated polymers were terminated with 2-propanol, carbon dioxide and deuterium oxide as mentioned in section 3.4.6. The resulting products were used in the following analyses.

G.p.c.

It was anticipated that the reaction of s-BuLi.TMEDA with SBR would be similar to that with a polydiene, equation (4.6), and therefore the addition of 2-propanol would effectively restore the SBR to its former unmetalated state by replacing the lithium at each 'activated' site with a proton. Samples metalated under the conditions given in table 3.14 and then reacted with 2-propanol were analysed by g.p.c. Each trace showed only one peak to be present, the molecular weight characteristics for which are given in table 4.6. The samples prepared in THF gave traces which were almost identical to that of the resolved main peak of the SBR starting material (figure 4.15) as shown by the g.p.c. trace for sample M1 in figure 4.17. The addition of s-BuLi.TMEDA causes complete breakdown of the star block material. The sharpness of the peaks indicates that the individual branch molecular weights are very close to those of their linear counterparts. This suggests that the branching process was carried out in situ rather than in a separate operation and blended with the linear material. The samples prepared in cyclohexane (M3 and M4) also show no trace of any star material remaining, however, compared to the THF prepared samples they have higher polydispersity values. This is
FIGURE 4.17
Gel permeation chromatogram of metalated SBR (sample M1)
clearly shown by the broadening of their g.p.c. curves (figures 4.18 and 4.19) especially in the lower molecular weight region. Some insight into why this occurs can be obtained from the colour changes which take place on initiator addition and also from the quantities used (table 3.14). In each preparation all reagents including TMEDA were added prior to s-BuLi addition. The reason why a several fold molar excess of TMEDA over the suggested 1:1 TMEDA:s-BuLi ratio is discussed later in section 4.6.2. In THF the gradual addition of s-BuLi initially did not produce any colour, then as more was added a faint pink colouration formed in the solution. The intensity did not change as further initiator was introduced. In cyclohexane, as with THF, no colouring occurred until a proportion of the initiator had been added and then the solution turned from a yellow to a deep red colour. This red intensified as further amounts were added. It has been observed by several workers (108, 110) that the n-BuLi.TMEDA metalation of polybutadiene in hydrocarbon solvent causes the solution to turn a deep red colour and therefore the similar colouration effects found with the present s-BuLi.TMEDA/SBR system suggests that metalation has to some extent occurred. The initial colourless period of s-BuLi addition could be due to impurities deactivating the initiator and also a reaction between initiator and linking agent producing linear polymer. The amount of initiator required to colour the solution was very small and varied in each preparation which implied that impurities were a contributing factor. The yellow colouration was either due to the s-BuLi.TMEDA complex or was an indication of low metalation levels. As with cyclohexane the colourless period observed with THF was attributed to impurities and a reaction with the linking agent. It is known (230) that small amounts of organic acids added to the SBR readily cause the breakdown of the star material to linear polymer.

In view of the ill defined solution colouration when using THF and
**FIGURE 4.18**
Gel permeation chromatogram of metalated SBR (sample H3)

**FIGURE 4.19**
Gel permeation chromatogram of metalated SBR (sample H4)
the effects a polar solvent may have on the formation of the s-BuLi.TMEDA complex it is possible that little or no metalation takes place. The use of THF as the solvent in which to carry out metalation is discussed further in section 4.7.2. The sharpness of the g.p.c. traces of the THF prepared samples in comparison to those obtained for the samples prepared in cyclohexane is a further indication that the same process is not occurring in both solvents.

It is possible that metalation is accompanied by a small amount of backbone degradation which explains the low molecular weight tail obtained with sample M3. As the amount of initiator is increased then the amount of degradation may also increase and as we can see with sample M4 (figure 4.19), where a very large amount of s-BuLi and (TMEDA) has been used, a large low molecular weight tail is produced and a noticeable drop in $M_n^*$ occurs (table 4.6). Comparing samples M2 (THF) and M3 (cyclohexane) where similar amounts of s-BuLi have been used, the total absence of any broadening effects in the former sample is unusual if the same process occurs in both solvents. Several assumptions have been made in this comparison which should not be overlooked. It is possible that differences in various experimental parameters, such as SBR concentration, [TMEDA]/[s-BuLi] ratio and metalation time, may influence the reactions taking place and therefore the range of parameters used in the present systems makes it difficult to draw firm conclusions. For this reason the effects of experimental variables on the metalation reactions are carefully considered in each of the SBR graft copolymer systems. It is also possible that when using THF as solvent the metalation sites of SBR may be different from those in cyclohexane and also less susceptible to backbone degradation. It will however be shown later (section 4.7.2) that using THF only as solvent no evidence for the grafting of SBR could be obtained. This suggests that if metalation does occur in THF polymerisation of monomer from these initiator sites does not proceed.
Backbone degradation has been observed by several workers (109, 110) when polydienes are metalated with n-BuLi.TMEDA at 50°C. In the present work, degradation was not considered a serious problem because in most cases the amounts of initiator used were less than the 35 moles/10^{-5} g SBR used with samples M3 in which g.p.c. broadening was just noticeable. The amounts of initiator used were based on a calculated number of graft sites, the above mentioned quantity corresponds to 41 sites per polymer chain. The reasons why the number of sites per chain should be a lot less than this are discussed in section 4.11.

**NMR**

The $^1$H NMR spectrum obtained for sample M3 was almost identical to that obtained for the unmetalated SBR. Using the same procedure as mentioned in section 4.4.1, the relative amounts of styrene and butadiene 1,4- and 1,2-addition units are given in table 4.8. There is very little difference between these results and those obtained for untreated polymer and therefore metalation does not appear to have any noticeable detrimental effects on backbone structure.

**Osmometry**

It was mentioned in section 4.4.1 that absolute molecular weight values for SBR can not be determined from g.p.c. without calibration data for that particular polymer and therefore osmometry was used to determine $M_n$. Using the method described in section 3.6, an $M_n$ value of 117,000 was obtained for sample M3 which had an $M_n^*$ (polystyrene $M_n$ equivalent) of 159,000 (table 4.8). A conversion factor of 0.74 is therefore required to convert $M_n^*$ to $M_n$. It is generally expected that the g.p.c. polystyrene equivalent ($M_n^*$) will be larger than the true value because polybutadiene has an $[<r_2^2>/N]^{1/2}$ value larger than that for polystyrene which means that for the same $V_R$ value (same % TPE path length position)
polystyrene will have a higher molecular weight than polybutadiene. To illustrate this point imagine SBR to be an AB block copolymer rather than a random copolymer, with a styrene content of 25\% wt. Taking a value of $[\langle r^2 \rangle/M]_n^{1/2}$ for polybutadiene of approximately $9.3 \times 10^{-2}$ nm (127) and applying equations (2.56) and (2.57) we obtain a conversion factor of 0.6 i.e. $0.6M_n^* = M_n$ for the AB block copolymer.

The above conversion factor, of 0.74, found for converting SBR polystyrene equivalents to true values cannot be used for SBR graft copolymers g.p.c. values because $M_n^*$ will vary with structure as well as composition, as mentioned in section 4.2.1 for the grafting of polyisoprene.

4.4.3 Metalation position

For a polymer such as SBR with the following structural units present (as identified by NMR, see table 4.8)

\[
\text{CH}_2-\text{CH}==\text{CH}-\text{CH}_2-\text{CH}==\text{CH}-\text{CH}_2-\text{CH}\ 
\]

there are several potential metalation sites. It was shown by Minoura et al. (108) that metalation of 1,4-polybutadiene occurs $\alpha$ to the double bond, i.e. in the allylic hydrogen position. For similar reasons of charge delocalisation the most likely position for metalation to occur in 1,2-polybutadiene is also $\alpha$ to the double bond. The metalation of polystyrene with BuLi.TMEDA systems has been the subject of several studies (107, 113, 225, 226, 232-234). There is, however, some uncertainty regarding the position of lithiation with benzilic, ortho, meta and para substitution positions each having been identified as the major positions.
To obtain information on the preferred metalation positions in the present copolymer system a metalated SBR sample (H6) was terminated with carbon dioxide as mentioned in section 3.4.3.3. The carboxylation conditions were chosen (60) so that the amount of coupling (equation (2.25)) was kept to a minimum. A g.p.c. trace taken of the completely soluble product was similar to that given in figure 4.18 and therefore no substantial amounts of coupled polymer were present. Analysis of this polymer containing -COOH groups was carried out using infrared and ultraviolet spectroscopy. Sections of the infrared spectra for carboxylated SBR (H6) and unmetalated SBR are given in figure 4.20. The presence of a broad band at approximately 1700 cm\(^{-1}\) wavenumbers in the H6 spectrum but absent in the parent polymer clearly indicates the presence of a carbonyl group in the structure. The resolution of peak position was, however, insufficient to distinguish aromatic from backbone substituents. Similarly, poorly defined peaks in the 900 to 750 cm\(^{-1}\) wavenumber range prevented the identification of possible aromatic substitution positions.

Ultraviolet absorption spectra were obtained for the above samples in chloroform (1.0 g/1\(^{-1}\)). The two spectra were superimposable at a wavelength of 260 nm and above (figure 4.21). The differences arising below 260 nm can be related to the amount of carboxylated material present in sample H6, as represented by the dashed line shown. Non-conjugated carboxylic acid systems absorb at low wavelengths (\(\lambda_{\text{max}} \leq 205\) nm) and have very small molar extinction coefficients (\(\varepsilon_{\text{max}} \leq 2 \times 10^2\)) whereas conjugated systems involving carboxylic acid groups, which in this particular case refer to aromatic substituents only, generally absorb at longer wavelengths (\(\lambda_{\text{max}} \geq 230\) nm) and have much higher values of \(\varepsilon_{\text{max}}\) (approximately \(10^4\)). From the peak height, absorbance (Ab), at 245 nm we can determine the amount of aromatic carboxylation from the relationship,
FIGURE 4.20
Infrared spectra of carboxylated SBR (sample M6) and unmetalated SBR (Solprene 1204)
FIGURE 4.21
Ultraviolet spectra for carboxylated SBR (sample N6) and unmetalated SBR (Solprene 1204)
Ab = C I \epsilon_{\text{max}} \quad (4.15)

where \(C\) is the concentration (moles \(1^{-1}\)) and \(L\) is the cell length (1 cm). Taking a value of \(\epsilon_{\text{max}} = 10^4\) (benzoic acid, \(\lambda_{\text{max}} = 230\)) we obtain a concentration of \(3.8 \times 10^{-5}\) moles \(1^{-1}\) for the \(-\text{COOH}\) containing units.

If SBR contains approximately 25% wt. styrene as suggested from NMR results (table 4.8) then for a solution concentration of 1 gl\(^{-1}\) there will be \(2.4 \times 10^{-3}\) moles \(1^{-1}\) of styrene present. Therefore, these results suggest that 1.6% of the styrene units present in SBR are carboxylated.

The maximum amount of styrene that can be carboxylated (based on a s-BuLi concentration of 18.2 moles/10\(^{-5}\) g SBR) is only 7.6%, therefore of the total amount of carboxylation possible 21% occurs in aromatic positions with the rest presumably occurring in SBR backbone positions. This treatment is, however, based on several assumptions:

a) absorption above 260 nm is unaffected by carboxylation
b) the molar extinction coefficient for the carboxylated aromatic species is the same as that for benzoic acid
c) only monosubstitution of styrene aromatic rings occurs
d) carboxylation occurs at all metalation sites.

Assumptions a) and c) are considered acceptable in view of the small amount of aromatic carboxylation that takes place. The choice of \(\lambda_{\text{max}}\) as suggested by b) may, however, vary slightly because a di- rather than monosubstituted benzene derivative will actually be formed and the value of \(\lambda_{\text{max}}\) will then depend on the position of the \(-\text{COOH}\) group relative to the backbone attachment position. For the various positions possible \(\lambda_{\text{max}} = 10^4 + 2 \times 10^3\) and therefore taking this range of values into account we obtain a value of 21 \(\pm\) 5% for the amount of carboxylation occurring in aromatic positions. This is still however based on the assumption that all metalation sites are carboxylated (d). To determine
the amount of carboxylation the following quantitative evaluation (236) was carried out. An accurately weighed amount (0.50 g) of carboxylated SBR (M₆) was dissolved in dry pyridine (100 cm³) and then a 10 cm³ aliquot of this solution titrated with standardised alcoholic potassium hydroxide (0.012 M) using phenolphthalein as indicator. The amount of base required to neutralise the solution was 0.61 cm³ which meant that in 10 cm³ of polymer solution there was 7.3 x 10⁻⁶ moles of -COOH. This compares with a value of 9.1 x 10⁻⁶ moles s-BuLi used in the metalation of the same quantity of polymer. These values are in reasonable agreement considering that some termination may have occurred during carboxylation as a result of other species being present in the solid carbon dioxide/TiF₅ slurry. It appears therefore that the amount of carboxylation is a good approximation of the true amount of metalation. Metalation studies (113, 226) which have shown that both backbone and aromatic substitution can occur indicate that backbone substitution occurs in only very small amounts (≪ 14%), therefore it is apparent that the metalation in the present SBR system is due largely to the presence of the butadiene units, but with approximately 20% occurring on the styrene ring.

Ultraviolet spectroscopy is not considered an ideal technique for determining the relative amounts of the different metalation positions because it can only be used to identify non-specific aromatic metalation and then only with respect to the expected total amount of metalation that occurs. A preferred technique would be the ^{13}C NMR analysis of SBR labelled with an identifiable group at each of the metalated sites. Preliminary ^{13}C NMR studies of deuterium (^2H) labelled SBR were carried out (section 3.6.2). The off-resonance ^1H spin decoupled spectra for metalated SBR terminated with deuterium oxide (M₅) and 2-propanol (M₃) are given in figure 4.22. The spectra are almost identical, however, it was anticipated that discernible differences would occur as a result of
Proton decoupled $^{13}$C NMR spectra of metalated SBH terminated with deuterium oxide (sample H5) and 2-propanol (sample H3)
the differences in nuclear spin quantum numbers for $^1H$ and $^2H$. The g.p.c. trace of the deuterated sample showed considerable broadening, similar to that shown in figure 4.19, as a result of the large amount of metalating agent used. This indicates that only a certain amount of metalation will occur before backbone degradation ensues. The use of $^2H$ does not produce a signal strong enough to be detectable at the particular metalation levels possible. Although no further work was carried out in this area it is apparent that to be able to detect the level of metalation present in the SBR systems some form of signal enhancement is required. A possible method would be to label the metalated SBR with $^{13}C$-enriched methyl iodide as used by Evans et al. (232) for the determination of the metalation positions in polystyrene.
4.5 **SBR GRAFTING - Definition of Terms Used**

It was mentioned in section 4.2.1 that g.p.c. techniques cannot be used to accurately determine changes in molecular weight or molecular weight distribution of a polymer on grafting and because only small differences were observed between grafted and ungrafted SBR g.p.c. traces, no such determinations were made. SBR graft copolymer molecular weights ($\bar{M}_n$) were obtained using osmometry techniques (section 3.6) and the results are discussed in section 4.10.3.

G.p.c. and yield information was, however, used for the determination of the various terms given below. These parameters are used throughout to describe the polymer products obtained in the SBR grafting reactions.

**Product Yield**

The yield of material polymerised is given by

$$\text{Yield (\%)} = \frac{\text{weight of product (g)} - \text{weight of SBR}}{\text{total weight of monomer}} \times 100$$ (4.16)

where samples were removed from the reactor prior to the weighing of the final product, appropriate corrections to the SBR and monomer weights were made.

**Grafting Efficiency**

Grafting efficiency (GE) is a measure of the effectiveness of a graft polymerisation and is given by (16)

$$\text{GE (\%)} = \frac{\text{polymer grafted (g)}}{\text{polymer grafted + homopolymer}} \times 100$$ (4.17)

where 'polymer grafted' refers only to the material which has been polymerised in the reaction. Using the expression in this form would
require a solvent extraction procedure to isolate the homopolymer present, however, using g.p.c. concentration calibration techniques (section 3.5.2.4) no isolation procedure is required. Expressing grafting efficiency in terms of concentrations

\[
GE (\%) = \frac{C_g}{(C_g + C_h)} \times 100
\]  

(4.18)

where \( C_g \) is the concentration (g/l) of polymer grafted and \( C_h \) the concentration of homopolymer. The linear plots obtained in figures 3.7, 3.8 and 3.9 show that g.p.c. detector response (expressed in arbitrary area units) is proportional to polymer concentration, therefore by measuring g.p.c. peak areas we can determine the concentration of various polymeric species for which calibration data is available.

When grafting efficiency is not 100% the presence of homopolymer in the g.p.c. trace of the graft copolymer product is very often clearly seen as a small peak at the low molecular weight side of the main SBR peak, as shown in figure 4.25. Taking polystyrene as an example, homopolymer concentration \( (C_h(PS)) \) can be given by

\[
C_h(PS) = \frac{A_2}{R_{PS}}
\]  

(4.19)

where \( A_2 \) is the area of the g.p.c. peak and \( R_{PS} \) the detector response constant for polystyrene and is equal to the gradient of the calibration plot given in figure 3.8. Substituting in a value of \( R_{PS} = 1.86 \) we get

\[
C_h(PS) = 0.54 A_2
\]  

(4.20)

Similarly an expression can be derived for the \( \alpha \)-methylstyrene homopolymer trace. The detector response constant for poly(\( \alpha \)-methylstyrene),
is obtained from figure 3.9. For a value of \( R_{PM3} = 2.10 \) we can derive an expression for the \( \alpha \)-methylstyrene homopolymer concentration \((C_{h(PMS)})\),

\[
C_{h(PMS)} = 0.48 A_2
\]  

(4.21)

where \( A_2 \) in this case is the g.p.c. peak area of \( \alpha \)-methylstyrene homopolymer.

Two methods were considered for the determination of \( C_g \):

a) Using the overall g.p.c. solution concentration \((C)\) we get

\[
(C_g + C_h) = FYC
\]  

(4.22)

where \( F \) is the weight fraction of monomer in the \((SBR + monomer)\) feed and \( Y \) is the fractional yield obtained from equation (4.16). Knowing \( C_h \) we can then obtain a value for \( C_g \) and hence the grafting efficiency.

b) Taking polystyrene as an example of the grafting polymer, the area of the main g.p.c. peak \((A_1)\) can be given by

\[
A_1 = R_{SBR} C_{SBR} + R_{PS} C_g(PS)
\]  

(4.23)

where \( R_{SBR} \) is the detector response constant for SBR and \( C_{SBR} \) the total SBR (grafted and ungrafted) concentration. \( C_{SBR} \) can also be given by

\[
C_{SBR} = C - (C_g(PS) + C_h(PS))
\]  

(4.24)

Substituting equation (4.24) into equation (4.23) and rearranging we get

\[
C_g(PS) = \left( \frac{R_{SBR}}{R_{SBR} - R_{PS}} \right) \left[ C - (C_h(PS) + \frac{A_1}{R_{SBR}}) \right]
\]  

(4.25)
From figure 3.7 $R_{SBR} = 1.47$, therefore substituting with values for $R_{PS}$ and $R_{SBR}$ we get

$$C_{g(PS)} = 3.77 \left[ (C_{h(PS)} + 0.68 A_1) - C \right]$$  \hspace{1cm} (4.26)

A similar expression can be derived for $\alpha$-methylstyrene using the $R_{PM}^5$ value,

$$C_{g(PMS)} = 2.33 \left[ (C_{h(PMS)} + 0.68 A_1) - C \right]$$  \hspace{1cm} (4.27)

$C_g$ and $C_h$ values can then be combined to determine grafting efficiency. Of the two methods for determining $C_g$, method b) would be preferred, theoretically, because concentration values are obtained using only one experimental technique whereas with method a) both product yield and g.p.c. data are used. However it was found that method b) was extremely sensitive to small errors in $A_1$, producing large variations in values of $C_g$. For this reason method a) was the adopted method for determining $C_g$ and subsequently grafting efficiency. It will be shown in section 4.10.1 that there is good agreement between this method and NMR for determining the amount of grafted polymer.

**Molecular Weight of Homopolymer Produced During Grafting**

Using the methods described in sections 3.5.2.2 and 3.5.2.3 the molecular weight parameters for several homopolymers, produced as the result of incomplete SBR grafting, are given in table 4.9. In nearly all cases the samples have very narrow molecular weight distributions as shown by the low uncorrected $\bar{M}_w/\bar{M}_n$ values given and as a result there is good agreement between the various molecular weight parameters used. Because $M_p(\text{obs})$ can be obtained direct from the polystyrene calibration
### TABLE 4.9
G.n.c. Results for Homopolymers Produced During sBR Grafting

<table>
<thead>
<tr>
<th>Sample ref.</th>
<th>Polymer</th>
<th>$\overline{M}_w$ (x 10(^{-3}))</th>
<th>$\overline{M}_n$ (x 10(^{-3}))</th>
<th>$M_p$ (obs) (x 10(^{-3}))</th>
<th>$M_p$ (theo) (x 10(^{-3}))</th>
<th>$\overline{M}_w / \overline{M}_n$</th>
</tr>
</thead>
<tbody>
<tr>
<td>G15</td>
<td>Polystyrene</td>
<td>3.4</td>
<td>3.1</td>
<td>3.3</td>
<td>3.2</td>
<td>1.10</td>
</tr>
<tr>
<td>G17</td>
<td>Polystyrene</td>
<td>3.9</td>
<td>3.5</td>
<td>3.7</td>
<td>3.7</td>
<td>1.11</td>
</tr>
<tr>
<td>G18</td>
<td>Polystyrene</td>
<td>6.4</td>
<td>5.5</td>
<td>6.1</td>
<td>5.9</td>
<td>1.16</td>
</tr>
<tr>
<td>G30</td>
<td>Poly((\alpha)-methylstyrene)</td>
<td>12.3</td>
<td>9.9</td>
<td>11.0</td>
<td>11.1</td>
<td>1.24</td>
</tr>
<tr>
<td>G34</td>
<td>Poly((\alpha)-methylstyrene)</td>
<td>21.4</td>
<td>17.8</td>
<td>17.0</td>
<td>19.5</td>
<td>1.20</td>
</tr>
<tr>
<td>G38</td>
<td>Poly((\alpha)-methylstyrene)</td>
<td>42.0</td>
<td>36.0</td>
<td>39.0</td>
<td>38.8</td>
<td>1.17</td>
</tr>
<tr>
<td>G39</td>
<td>Poly((\alpha)-methylstyrene)</td>
<td>24.1</td>
<td>21.1</td>
<td>22.0</td>
<td>22.6</td>
<td>1.14</td>
</tr>
<tr>
<td>G42</td>
<td>Poly((\alpha)-methylstyrene)</td>
<td>12.3</td>
<td>11.5</td>
<td>11.3</td>
<td>11.9</td>
<td>1.07</td>
</tr>
<tr>
<td>G46</td>
<td>Poly((\alpha)-methylstyrene)</td>
<td>24.2</td>
<td>20.5</td>
<td>19.1</td>
<td>19.6</td>
<td>1.18</td>
</tr>
<tr>
<td>G49</td>
<td>Poly((\alpha)-methylstyrene)</td>
<td>11.5</td>
<td>10.6</td>
<td>10.7</td>
<td>11.0</td>
<td>1.09</td>
</tr>
<tr>
<td>G68</td>
<td>Poly((\alpha)-methylstyrene- (\beta)-styrene)</td>
<td>15.1</td>
<td>13.9</td>
<td>14.0</td>
<td>14.5</td>
<td>1.09</td>
</tr>
</tbody>
</table>

**a)** Synthesis details:
- Table 3.5: G15, G17 and G18
- Table 3.8: G30, G34, G38 and G39
- Table 3.9: G42, G46 and G49
- Table 3.11: G68
curve (figure 3.6) it was considered a suitable parameter for representing homopolymer molecular weight. In all samples where homopolymer is present in the g.p.c. trace of the graft copolymer, the molecular weight is given as an $M_p(\text{obs})$ value. It will be shown in section 4.10.2 that homopolymer and grafted polymer have very similar molecular weights and therefore the $M_p(\text{obs})$ values quoted are effectively the molecular weights of the grafts in the SBR graft copolymer.

**Calculated Graft Molecular Weight**

The calculated graft (and homopolymer) molecular weights were obtained from the product of $Y \times \bar{M}_s$, where $Y$ is the fractional yield obtained from equation (4.16) and $\bar{M}_s$ is the stoichiometric number average molecular weight and is given by

$$\bar{M}_s = \frac{\text{weight of monomer(g)}}{\text{moles initiator}}$$

(4.28)

This equation is analogous to equation (2.22).

**Average Number of Grafts per Chain**

As shown in footnote d), table 3.1 the average number of graft sites per chain ($A$) can be obtained from the product of the backbone molecular weight and initiator concentration. In the SBR systems the graft molecular weight information obtained from the homopolymer $M_p(\text{obs})$ values enables the average number of grafts per chain ($A'$) to be determined. Taking the SBR backbone molecular weight as $\bar{M}_n = 117,000$ (see section 4.10) the following expression is derived

$$A' = \frac{1.17 \times \bar{M}_s \times [s-\text{BuLi}] \times CE}{M_p(\text{obs})}$$

(4.29)

where $[s-\text{BuLi}]$ is the initiator concentration (moles/$10^{-5}$ $\mu$ SBR).
4.6 POLYSTYRENE AND SBR-g-POLYSTYRENE

The apparent ease with which polyisoprene could be grafted with styrene (section 4.2) suggested that styrene was a suitable monomer for investigating the extent of SBR grafting under different experimental conditions. Initial studies of solvent and TMEDA effects on polymer product were carried out with styrene homopolymer.

4.6.1 Homopolymer Studies

All homopolymer g.p.c. molecular weight parameters were determined as mentioned in sections 3.5.2.2 and 3.5.2.3. \( M_p(\text{obs}) \) values were obtained direct from the polystyrene calibration trace (figure 3.6). Product yield and g.p.c. data for polystyrene samples prepared in cyclohexane and THF are given in table 4.10. Considering the cyclohexane preparation (H4) a narrow molecular weight distribution polymer in high yield was obtained. The large difference between \( M_n \) and the calculated molecular value suggests that a proportion of the initiator has been terminated by impurities, this may account for the small low molecular tail found on the g.p.c. trace (figure 4.23). For the experimental conditions employed (table 3.3) the presence of TMEDA does not appear to have any detrimental effects on the polymer product.

Polystyrene samples prepared in THF with or without TMEDA present give very broad bimodal g.p.c. traces, a typical example is given in figure 4.23. The differences between the peak heights and peak positions for the two polymers given in table 4.9 and for others prepared in this solvent suggest there is no definite relationship between the two peaks in terms of their relative concentrations or molecular weights. As mentioned in section 2.1.2. the polymerisation of styrene in polar solvent proceeds via unassociated chain ends in the form of both ion pairs and free ions, from literature values of \( k^+ \), \( k^- \) and \( K_I \) for polyl
### TABLE 4.10

<table>
<thead>
<tr>
<th>Sample ref.</th>
<th>calc. mol. wt.</th>
<th>$\bar{M}_n$ (x 10^{-3})</th>
<th>$\bar{M}_p$(obs) (x 10^{-3})</th>
<th>$\frac{\bar{M}_w}{\bar{M}_n}$</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H4</td>
<td>2.4</td>
<td>11.1</td>
<td>12.3</td>
<td>1.15</td>
<td>98</td>
</tr>
<tr>
<td>H2</td>
<td>8.6</td>
<td>-</td>
<td>90.0</td>
<td>4.6</td>
<td>-</td>
</tr>
<tr>
<td>H3</td>
<td>10.5</td>
<td>252.0</td>
<td>380.0</td>
<td>2.01</td>
<td>96</td>
</tr>
</tbody>
</table>

a) For synthesis details see table 3.3.

b) Calculated polystyrene molecular weight = Yield x $[s-$BuLi$]^{-1}$

where $[s-$BuLi$]$ is the initiator concentration (moles/g monomer).

c) Yield (%) = \frac{weight \ of \ polymer \ (g)}{initial \ weight \ of \ monomer} \times 100
FIGURE 4.2
Gel permeation chromatograms of polystyrene prepared in cyclohexane (sample H4) and THF (sample H3)
styryllithium in THF at 25°C (4/4) and using equations (2.11) and (2.17) the polymerisation rates obtained for the present systems are such that complete conversion of styrene to polymer should occur in several seconds, but in practice 5 minutes is more typical. The very fast initiation and propagation reactions and the finite time required to inject the initiator into the monomer solution may account for the molecular weight broadening observed with the g.p.c. traces but not for the bimodal distribution. The data obtained for the resolved main peak of sample H3 shows poor agreement between $\bar{M}_n$ and $M_p(\text{obs})$ values, as would be expected for a broad molecular weight distribution polymer (see section 4.2.2).

The bimodal molecular weight distributions are probably a consequence of the fast polymerisation rate. If we assume there is always a certain amount of impurity material present in the solution, as shown by the differences between the actual and calculated molecular weights, then it is possible that on initiator addition a certain amount of polymeric material forms before the impurities can deactivate the 'living' chain ends. When a hydrocarbon solvent is used this has the effect of producing a low molecular weight 'tail', however when THF is the solvent the reaction rates are so fast that this 'tail' may actually form a separate broad peak, the size of this low molecular weight being determined by the amount of deactivating material present.

It may be possible to overcome these broadening and bimodal molecular weight distribution problems by using 'seeding' techniques, where a very small amount of monomer is added to the reactor containing the solvent and initiator, this is then allowed to react for a few seconds before the bulk of the monomer is added. This method effectively splits the initiation and propagation reactions and also deactivates the impurity species prior to monomer addition. As this is analogous to anionic grafting methods where the monomer is added to the initiated backbone polymer
solution, the experimental techniques used in the present preparations were only employed to ensure polymerisation did occur, i.e. initiator was added until a permanent colour formed in the solution. As mentioned earlier it was the intention in these preparations to investigate the effects of TMEDA on the polymer products and from the results given in table 4.10 its presence does not appear to have any detrimental effects on the anionic polymerisation of styrene in THF.

Another feature of these THF polymerisations is the apparent colour changes which occur, initially the polystyryllithium solution was a light red colour, however after several hours the colour began to fade until it finally turned colourless. In cyclohexane the polymer solution remained a deep red colour throughout the polymerisation period, only turning colourless when alcohol was added to terminate the reaction. Initial solution colour differences between cyclohexane and THF systems can probably be attributed to solvation effects which only occur, to any appreciable extent, in the latter solvent. Colour fading was observed with all polymerisations at room temperature where THF was the only solvent used. At first this effect was attributed to the gradual 'killing off' of the polymer solution, however, in view of the THF drying procedure which utilises a living polymer system as a purity check and the similarity in experimental conditions between the THF and cyclohexane preparations, it seems unlikely that such a premature termination process should only occur in THF. A possible explanation is that the living polymer undergoes a slow transformation reaction of the type suggested by Szwarc (222) for polystyrylsodium in THF (equations (4.7) and (4.8)) or alternatively the living polymer reacts directly with the solvent. Rembaum (237) has shown that ethyllithium can react with THF in the following way:

\[ \text{C}_2\text{H}_5\text{Li} + \text{THF} \rightarrow \text{C}_2\text{H}_5(\text{CH}_2)_{4}\text{O}^- \text{Li}^+ \]  

(4.30)
It is apparent that a similar reaction could occur between polystyryllithium and THF.

\[
\sim \text{CH}_2\text{CHLi}^+ + \text{THF} \rightarrow \sim \text{CH}_2\text{CH(CH}_2\text{H}_4\text{O}^-\text{Li}^+ \quad (4.31)
\]

This has been confirmed by Fetters (238), who attributed solution viscosity increases in the polystyryllithium/THF system, after standing for 24 hours, to associations not of the polystyryllithium species but of lithium alkoxide chain ends.

Because the formation of the dormant \(\sim \text{CH}_2\text{O}^-\text{Li}^+\) end group proceeds very slowly at room temperature, complete conversion of monomer to polymer occurs prior to this reaction taking place and therefore the yield is unaffected. In the present preparations solution colour changes were noticeable after several hours which suggests that the changes were due to a reaction between polystyryllithium and THF rather than a transformation type reaction because these latter reactions only occur when the solutions have been standing for several days (222).

4.6.2 Grafting in Cyclohexane

Using the terms listed in section 4.5 the results for the various preparations in cyclohexane are given in table 4.11. When no homopolymer was present in the g.p.c. trace of the product, e.g. figure 4.24, grafting efficiency was taken as approximately 100%, an exact value could not be quoted because of the difficulties in distinguishing very small amounts of homopolymer (< 2%) from baseline fluctuations in the g.p.c. trace. When grafting efficiency was not 100% and homopolymer was clearly in evidence, g.p.c. traces similar to that given in figure 4.25 were obtained.

Two groups of experiments were carried out to investigate the effects
<table>
<thead>
<tr>
<th>Sample ref.</th>
<th>Yield (%)</th>
<th>GE (%)</th>
<th>homopolymer M_p (obs) (x 10^{-3})</th>
<th>calc. graft mol. wt. (x 10^{-3})</th>
<th>A'</th>
</tr>
</thead>
<tbody>
<tr>
<td>G10</td>
<td>89</td>
<td>~100</td>
<td>-</td>
<td>6.2^b</td>
<td>(8.6)^b</td>
</tr>
<tr>
<td>G11</td>
<td>84</td>
<td>~100</td>
<td>-</td>
<td>2.2</td>
<td>(18.8)</td>
</tr>
<tr>
<td>G12</td>
<td>72</td>
<td>~100</td>
<td>-</td>
<td>0.5</td>
<td>(18.6)</td>
</tr>
<tr>
<td>G13</td>
<td>55</td>
<td>~100</td>
<td>-</td>
<td>0.8</td>
<td>(18.7)</td>
</tr>
<tr>
<td>G14</td>
<td>96</td>
<td>~100</td>
<td>-</td>
<td>5.8</td>
<td>(18.8)</td>
</tr>
<tr>
<td>G15</td>
<td>80</td>
<td>83</td>
<td>3.3</td>
<td>4.4</td>
<td>15.2</td>
</tr>
<tr>
<td>G16</td>
<td>86</td>
<td>97</td>
<td>3.6</td>
<td>4.8</td>
<td>17.8</td>
</tr>
<tr>
<td>G17</td>
<td>83</td>
<td>77</td>
<td>3.7</td>
<td>2.8</td>
<td>13.4</td>
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<td>G18</td>
<td>94</td>
<td>90</td>
<td>6.1</td>
<td>7.8</td>
<td>10.8</td>
</tr>
<tr>
<td>G19</td>
<td>93</td>
<td>95</td>
<td>7.8</td>
<td>7.6</td>
<td>8.7</td>
</tr>
<tr>
<td>G20</td>
<td>79</td>
<td>89</td>
<td>10.0</td>
<td>6.6</td>
<td>5.2</td>
</tr>
<tr>
<td>G21</td>
<td>94</td>
<td>94</td>
<td>4.8</td>
<td>7.8</td>
<td>14.2</td>
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<tr>
<td>G22</td>
<td>95</td>
<td>1700</td>
<td>1.4</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>G23</td>
<td>74</td>
<td>82</td>
<td>5.3</td>
<td>2.9</td>
<td>6.0</td>
</tr>
</tbody>
</table>

Values in ( ) are average number of graft sites per chain (A), A = 1.17 [s-BuLi] where [s-BuLi] is the initiator concentration (moles/10^{-5} g SBR).

a) For synthesis details see tables 3.5 (G10-G21) and 3.6 (G22 and G23).
b) Based on the total rather than the 'active' amount of initiator added.
Differential Refractive Index

Gel permeation chromatogram of Styr-E-poly styrene (sample G13)
of metalation time (G15-G17) and [TMEDA]/[n-BuLi] molar ratio (G18-G21) on grafting efficiency. The results, given in table 4.11, are shown graphically in figure 4.26.

Considering the metalation time results, a high grafting efficiency ( > 95%) was achieved when the metalation reaction was allowed to proceed for 17 hours. However, only moderate efficiencies (approx. 80%) were obtained for metalation times of up to 5 hours. Despite the shortage of data in the 5 to 17 hours metalation time range it would appear that metalation times much greater than the 2 hours (at 20°C) suggested by Falk et al. (15) for the metalation of polyisoprene and polybutadiene, are required in the present SBH system. It was, however, later reported by Hadjichristidis and Hoovers (219) that some 20 to 28% homopolystyrene was present in the final product of the styrene grafting of polyisoprene using the same experimental conditions as those proposed by Falk. Homopolymer has also been obtained when n-BuLi.TMEDA was used as the metalating agent for the preparation of polyisoprene-g-polystyrene (109, 110). To account for the homopolymer formation Tate and coworkers (110) have suggested the following possibilities:

a) there may be chain transfer due to transmetalation of unreacted styrene by the metalated polydiene,

b) incomplete metalation of the backbone polymer may occur as the result of the presence of low molecular weight metalatable impurities capable of initiating polymerisation,

c) an equilibrium may exist between metalated polydiene and TMEDA which has itself been metalated by BuLi (239), the metalated TMEDA also being capable of initiating polymerisation,

d) small fragments formed by chain scission during metalation might initiate styrene polymerisations.

With regard to the metalation time experiments (G15-G17) the narrow
FIGURE 4.26
The effect of metalation time and \([\text{TMEDA}] / [\text{s-BuLi}]\) molar ratio on grafting efficiency for the preparation of SBR-g-polystyrene in cyclohexane.
molecular weight distribution homopolymers formed (table 4.9) suggest that a transmetalation reaction does not occur unless the transfer to monomer is extremely rapid. However, if such a fast reaction did occur then grafting efficiency would be almost independent of metalation time which does not appear to be the case in these experiments. Similarly, proposals b) and d) and others concerning irreversible side reactions would only produce narrow molecular weight distribution homopolymers if the reactions were extremely rapid, therefore grafting efficiency would not be expected to increase with metalation time. For an equilibrium state to exist as suggested in c) the equilibrium must be very close to 100% metalation of SBR and therefore can be regarded as an irreversible reaction. In summary it can be said that even from the limited data obtained it would appear that metalation of SBR increases with time and is therefore primarily a kinetic effect. For this reason all subsequent metalation reactions were carried out for periods in excess of 12 hours.

The results given in figure 4.26, show grafting efficiency to be independent of [TMEDA]/[n-BuLi] ratio in the range 1 to 50. As mentioned in section 2.1.1, Langer (37) suggested that BuLi and TMEDA formed a 1:1 complex in hydrocarbon solvent and that the complex was a very powerful metalating agent. This is consistent with kinetic data obtained for the n-BuLi,TMEDA metalation of polystyrene (225) and polybutadiene (108) where metalation rate increased as the \([\text{TMEDA}]/[\text{n-BuLi}]\) value was increased towards 1.0, at values above this the rate remained constant. Ultraviolet spectra obtained by Hay and coworkers (221) for the n-BuLi,TMEDA metalated polybutadiene system in hydrocarbon solvent suggested that the active species were TMEDA separated ion pairs in which one lithium ion was tetrahedrally co-ordinated to two molecules of TMEDA. This would imply that a \([\text{TMEDA}]/[\text{n-BuLi}]\) value of 2.0 is the preferred complex ratio. It was not the intention in the present preparations (G18-G21) to establish
a lower [TMEDA]/[s-BuLi] ratio with which efficient metalation and sub­sequently high grafting efficiency could be achieved in the allocated time (13 hours), moreover, the objective was to determine whether TMEDA in excess amounts, with respect to s-BuLi, would have a detrimental effect on grafting efficiency and as the results show, no such effects occur. TMEDA was used in amounts in excess of the 1.0 or 2.0 molar ratio in most SBR grafting reactions because it was found that it reduced solution viscosity considerably during metalation and grafting. This suggests that even in the presence of TMEDA chain associations occur and it is only when large amounts of this chelating agent are added that these associations are broken up. The similarity between homopolymer and grafted polymer molecular weight, as indicated in section 4.10.2, suggests that grafting efficiency will not affect the overall polymer yield. The results for the two groups of preparations mentioned above (G15-G17 and G18-G21) confirm this.

A third group of SBR-g-polystyrene preparations (G11-G14) was carried out to study the effects of varying the monomer feed (see table 3.5). Using a [TMEDA]/[s-BuLi] ratio of 8.3 and a metalation time of 14.5 hours the grafting efficiencies were all taken as approximately 100% (table 4.11) as suggested by the complete absence of any detectable homopolymer in the g.p.c. traces. The amount of monomer did not therefore have an effect on grafting efficiency. Because of the problems mentioned earlier of detecting very small amounts of homopolymer a 10% wt. styrene feed was taken as the lower limit. Final product yields were determined using equation (4.16) and also by NMR using the method mentioned in section 4.4.1. The NMR values were close to the initial feed amounts which suggests almost complete conversion of monomer to polymer. The yields given in table 4.11 show a large amount of scatter especially for the low styrene content polymers. This may have been due to small weight differences occurring
as the result of incomplete precipitation of polymer which would ultimately produce larger errors in the lower monomer feed samples, as found. The high yield obtained with sample G14 (styrene feed 47.5% wt.) suggests that, for the given precipitation technique, sample recovery may be more effective with the higher molecular weight samples. In view of the possibility of incomplete precipitation, the sample recovery procedure in all subsequent preparations was modified so as to include a second precipitation stage. This was carried out by pouring the supernatant liquor remaining from the first precipitation into a second quantity (x2 excess) of alcohol and then any precipitate that formed was allowed to settle before being extracted and added to the bulk amount.

4.6.3 Grafting Attempts in Other Solvents

Two preparations were attempted, one in THF (G22) and the other in methylcyclohexane/THF (G2J). The experimental conditions are given in table 3.6 and the g.p.c. and yield results obtained are given in table 4.11.

In the THF preparation a large amount of initiator was required to maintain colouration. The solution turned colourless 3 hours after styrene addition. Further additions of initiator, although turning the solution a pink colour again, did not produce further polymerisation, as evidenced by the identical g.p.c. traces. The product g.p.c. trace contained a very large homopolymer peak with a very high \( M_p(\text{obs}) \) value which suggests that little or no grafting has taken place and that large amounts of the initiator have been deactivated by THF or by impurities present in the solvent. The preparation does, however, show that styrene will still polymerise extremely rapidly in THF in the presence of SBR and TMEDA, as evidenced by the high yield obtained in a relatively short period of time.
For sample G23, metalation and polymerisation for 5.5 hours was conducted in methylcyclohexane with the THF only being added after this period. G.p.c. traces of samples taken before THF addition and at the end of the polymerisation period showed that homopolymer $\bar{H}_p(\text{obs})$ increased from 4,800 to 5,300, however, the relatively low yield compared to the cyclohexane systems suggests that the presence of the small amount of THF has not significantly improved the polymerisation rate. The grafting efficiency obtained was slightly lower than for $SBR-g$-polystyrene preparations in cyclohexane under similar conditions.
4.7 POLY(\(\alpha\)-METHYlstyrene) AND SBR-g-POLY(\(\alpha\)-METHYlstyrene)

Prior to the preparation of the SBR graft copolymers, several homopolymers were prepared to investigate the effects of various solvents on the polymer products.

4.7.1 Homopolymer Studies

Product yield and g.p.c. data for poly(\(\alpha\)-methylstyrene) samples prepared in various solvents and under various experimental conditions (table 3.4) are given in table 4.12.

No noticeable amounts of product were obtained when hydrocarbon solvents only were used (H5 and H6) which suggests that for the experimental conditions employed, the polymerisation rate must be almost nil. It has been found by other workers (228, 240) that \(\alpha\)-methylstyrene, compared to styrene, polymerises very slowly in hydrocarbon media.

Using THF as solvent (H7 and H8) or cosolvent with cyclohexane (H9) or methylcyclohexane (H10) high yields were obtained. For a mixed cyclohexane/methylcyclohexane system containing only small amounts of THF (H11 and H12) poor yields were obtained. This was probably because precipitation of polymer occurred during polymerisation. It is not unexpected that precipitation may occur because cyclohexane and methylcyclohexane are both theta solvents for \(\alpha\)-methylstyrene and the polymerisations were carried out at temperatures well below their theta values. THF, a good solvent for poly(\(\alpha\)-methylstyrene), was present in sufficient amounts to prevent precipitation occurring in the other mixed solvent systems mentioned.

In each of the preparations the monomer solutions turned bright red as soon as initiator was added. Preliminary studies of 'living' solutions held at room temperature indicated that no polymer product was obtainable at this temperature. We can therefore assume that only initiation occurs
### TABLE 4.12

G.p.c. and Yield Results for Poly(\(\alpha\)-methylstyrene)

<table>
<thead>
<tr>
<th>Sample ref.</th>
<th>calc. mol. wt. (\times 10^{-3})</th>
<th>(\bar{M}_n) (\times 10^{-3})</th>
<th>(M_p)(obs) (\times 10^{-3})</th>
<th>(\frac{\bar{M}_w}{\bar{M}_n})</th>
<th>Yield (c) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H7</td>
<td>11.5</td>
<td>10.0</td>
<td>11.2</td>
<td>1.41</td>
<td>90</td>
</tr>
<tr>
<td>H8</td>
<td>9.9</td>
<td>9.7</td>
<td>11.4</td>
<td>1.34</td>
<td>83</td>
</tr>
<tr>
<td>H9</td>
<td>17.2</td>
<td>15.0</td>
<td>16.0</td>
<td>1.17</td>
<td>86</td>
</tr>
<tr>
<td>H10</td>
<td>2.6</td>
<td>6.3</td>
<td>6.9</td>
<td>1.12</td>
<td>88</td>
</tr>
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<td>H11</td>
<td>8.1</td>
<td>9.0</td>
<td>9.5</td>
<td>1.12</td>
<td>52</td>
</tr>
<tr>
<td>H12</td>
<td>10.6</td>
<td>5.9</td>
<td>7.1</td>
<td>1.45</td>
<td>69</td>
</tr>
</tbody>
</table>

a) For synthesis details see table 3.4.

b) and c) As given in table 4.10.
at room temperature and that polymerisation commences only when the reactors are placed in the low temperature baths. The reasonable agreement between the actual and calculated molecular weight values suggests that very little of the initiator is 'killed off' on initiation. The low polydispersity values obtained for samples H9, H10 and H11 indicate that no appreciable termination effects have occurred during polymerisation.

The large $\bar{M}_w/\bar{M}_n$ value obtained for sample H12 can probably be attributed to the large amounts of polymer formed under heterogeneous conditions (see figure 4.37). The amount of material formed heterogeneously in preparation H11 was, however, insufficient to affect the overall molecular weight distribution.

The preparations carried out in THF, H7 and H8, both gave polymers with broad distributions. Unlike the polystyrene preparations (section 4.6.1) the broadening cannot be attributed to an overlap between the initiation and propagation reactions because initiation was carried out at room temperature and, as mentioned above, no appreciable amounts of polymer form at this temperature. The separation of the initiation and propagation reactions may, however, account for why no bimodal g.p.c. traces were obtained with the $\alpha$-methylstyrene polymerisations. Typical g.p.c. traces for samples prepared in THF and a hydrocarbon/THF solvent system are given in figure 4.27. Considering other possible reasons for the molecular weight broadening obtained with the THF prepared samples, it seems unlikely that premature termination is the primary cause in view of the persistence of the deep red 'living' polymer solution colouration throughout the polymerisation. A reaction of the type given in equation (4.31) is also unlikely because the formation of lithium alkoxide species does not occur at low temperature (44). It is also unlikely that initiation is incomplete at room temperature in view of the rapidity with which the solutions turned deep red on initiator addition and also because the reactors were held at room temperature for several minutes prior to
FIGURE 4.27
Gel permeation chromatograms of poly($\alpha$-methylstyrene) prepared in THF (sample H7) and cyclohexane/THF (sample H9)
to immersion into the low temperature baths. Molecular weight broadening may be related to the initial fast propagation rates observed when preparations are carried out in THF or high THF containing systems (see section 4.7.6). If insufficient solution mixing occurs during this period of rapid propagation or a temperature gradient occurs in the solution as the reactors are cooled to the working temperature it is possible that because of these non-ideal conditions (section 2.3.1) molecular weight broadening ensues. The kinetics of the preparations are discussed in section 4.7.6.

In summary, narrow molecular weight distribution polymers in high yield can be prepared in hydrocarbon solvent at -35 and -78°C provided THF is present and in sufficient quantities (>10% vol.) to prevent the polymer precipitating from solution at that temperature.

4.7.2 Unsuccessful Grafting Attempts

Several solvent systems were used in which no grafting or polymerisation would occur, these were; THF, methylcyclohexane and methylcyclohexane/cyclohexane.

THF

The yield and g.p.c. data obtained for samples prepared using the experimental conditions given in table 3.7 indicated that no grafting or homopolymer formation had occurred. During the metalation period the solutions turned from an initial yellow colour to a faint pink colour within several minutes. The addition of α-methylstyrene and the immersion of the reactors into the low temperature baths caused the colour to fade quickly until the solutions finally turned colourless. To eliminate the possibility of initiator being 'killed off' by impurities large amounts of s-BuLi were used in each preparation. Therefore,
assuming impurity deactivation is not totally responsible for the lack of poly(α-methylstyrene) product, the faint metalation colour, although not conclusive, suggests that a reaction occurs between THF and initiator or lithiated polymer sites producing non-α-methylstyrene initiating species. This reaction may continue throughout the preparation until the solution finally turns colourless, with the addition of α-methylstyrene accelerating this process by introducing further deactivating materials.

Summarising all the results for the attempted preparations in THF of polystyrene, poly(α-methylstyrene), SBR-g-polystyrene and SBR-g-poly-(α-methylstyrene), we can say that the prolonged exposure of s-BuLi or other initiating species to THF causes partial or total loss of their activity towards further initiation and polymerisation. The extent of SBR metalation, if it occurs at all in THF, is questionable (see section 4.4.2). The formation of the s-BuLi.TMEDA complex may be prevented by the solvating effect of the THF on the initiator. The reactivity of this solvated species may not then be sufficient to metalate the SBR backbone. The obvious complexity of the metalation and grafting process and the poor results obtained when THF is the solvent suggests that THF should not be used as the major solvent in which to carry out the grafting reactions. No further preparations were attempted in a pure THF system. In addition to the drawbacks mentioned above when using THF as solvent and its possible reaction with polystyryllithium over long periods of time (see equation (4.1)), it has also been reported (238) that living polymers of polyisoprene and polybutadiene are also gradually terminated by THF. A reaction similar to that reported by Rembaum (237) occurs:

\[
\text{H-Li + THF} \rightarrow \text{H-H} + \begin{array}{c}
\text{H}_2\text{C} \\
\text{H}_2\text{C}
\end{array} \begin{array}{c}
\text{Li} \\
\text{H}
\end{array} \\
\text{O} \begin{array}{c}
\text{CH}_2
\end{array}
\] (4.32)
where R-Li is the polymer-lithium species. This would imply that metalated polymer could also react with THF.

**Methylcyclohexane**

It has already been shown (sample H5) that \(\alpha\)-methylstyrene will not polymerise to any appreciable extent in this solvent using the conditions given in table 3.4. However, the importance of being able to graft \(\alpha\)-methylstyrene in a single hydrocarbon solvent warranted further investigation into this particular system which does not freeze at \(-78^\circ\text{C}\). Several grafting reactions were attempted in this solvent using the various experimental conditions given in table 3.7. The bright red solution colouration during the metalation period confirmed that metalation to some extent does occur. The range of polymerisation conditions used, i.e., 8 to 24 hours at \(-35^\circ\text{C}\) and 24 to 72 hours at \(-78^\circ\text{C}\) were not sufficient to produce any poly(\(\alpha\)-methylstyrene). If polymerisation does occur in this solvent the reaction rates are, for practical purposes, prohibitive and no further preparations in this single hydrocarbon solvent system were attempted.

**Methylcyclohexane/cyclohexane**

Although an attempt at polymerising \(\alpha\)-methylstyrene in this solvent system had also been unsuccessful (sample H6), an attempt to actually graft \(\alpha\)-methylstyrene from SBR was carried out at a higher temperature and for an extended polymerisation period (sample G56, table 3.10). Yield and g.p.c. trace data confirmed that no poly(\(\alpha\)-methylstyrene) in any measurable quantity was produced. Further attempts were not carried out in view of the fact that if polymerisation did occur in these hydrocarbon solvents solubility problems, of the kind found with the homopolymer preparations (H11, H12), might also occur with the graft copolymer systems and therefore poor yields and broad molecular weight distributions would ensue.

It is apparent that \(\alpha\)-methylstyrene polymerisation will always need
to be promoted by a polar solvent and that other species such as TMEDA in small quantities are not sufficient, as found in section 4.7.1.

4.7.3 Grafting in Cyclohexane/THF

Table 4.13 gives the g.p.c. and yield results for the SBR-g-poly-(α-methylstyrene) samples prepared in cyclohexane/THF under various experimental conditions (table 3.8). The g.p.c. traces of the products were similar to those obtained for SBR-g-polystyrene (figure 4.25) except that the homopolymer peaks were generally found at higher molecular weight and therefore often partially merged with the main peak, a typical example (G39) is given in figure 4.28.

Metalation conditions which can possibly affect the grafting efficiency in a particular solvent are: SBR concentration, s-BuLi concentration, [TMEDA]/[s-BuLi] ratio, metalation temperature and metalation time. The actual range of SBR concentration values that can be used is very limited because above 5% w/v the solutions become too viscous to stir and below 1% w/v very large reactors are required if sufficient quantities of material are to be made for testing purposes. Within this small range it would be very difficult to monitor concentration effects. On viscosity grounds it would be anticipated that metalation would occur at a faster rate in the more dilute solution. Two samples, G38 and G39, prepared under identical conditions except for their SBR concentrations of 4.7 and 2.9% w/v, respectively, gave results to the contrary, i.e. the higher grafting efficiency value was obtained with the more concentrated solution. The values were, however, fairly low and the fact that although the concentration of s-BuLi with respect to SBR was the same in each preparation, the actual amounts of initiator (and TMEDA) present were different and therefore the results were not considered significant. SBR concentrations in all the other preparations were kept within the range 1 to 3% w/v for
### Table 4.13

G.n.c. and Yield Results for 388-g-poly(α-methylstyrene)
Prepared in Cyclohexane/THF

<table>
<thead>
<tr>
<th>Sample ref.</th>
<th>Yield (%)</th>
<th>G5 (%)</th>
<th>homopolymer $M_p$ (obs) ($\times 10^{-3}$)</th>
<th>calc. graft mol. wt. ($\times 10^{-3}$)</th>
<th>$A'$</th>
</tr>
</thead>
<tbody>
<tr>
<td>G30</td>
<td>73</td>
<td>51</td>
<td>11.0</td>
<td>11.4</td>
<td>4.1</td>
</tr>
<tr>
<td>G31</td>
<td>35</td>
<td>~65$^b$</td>
<td>25.0</td>
<td>2.9</td>
<td>1.0</td>
</tr>
<tr>
<td>G32</td>
<td>32</td>
<td>71</td>
<td>7.2</td>
<td>1.0</td>
<td>3.7</td>
</tr>
<tr>
<td>G33</td>
<td>80</td>
<td>77</td>
<td>46.0</td>
<td>9.0</td>
<td>1.0</td>
</tr>
<tr>
<td>G34</td>
<td>48</td>
<td>74</td>
<td>17.0</td>
<td>4.0</td>
<td>2.2</td>
</tr>
<tr>
<td>G35</td>
<td>13</td>
<td>~70$^b$</td>
<td>9.3</td>
<td>1.1</td>
<td>1.1</td>
</tr>
<tr>
<td>G36</td>
<td>36</td>
<td>~80$^b$</td>
<td>9.3</td>
<td>3.0</td>
<td>3.6</td>
</tr>
<tr>
<td>G37</td>
<td>11</td>
<td>~70$^b$</td>
<td>10.0</td>
<td>0.9</td>
<td>0.8</td>
</tr>
<tr>
<td>G38</td>
<td>90</td>
<td>70</td>
<td>39.0</td>
<td>7.9</td>
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<td>G39</td>
<td>79</td>
<td>54</td>
<td>22.0</td>
<td>6.9</td>
<td>1.5</td>
</tr>
</tbody>
</table>

---

a) For synthesis details see table 3.8.

b) Approximate values are given for low yield samples where g.p.c. peak resolution was poor or small amounts of gel material were present in the product.
Differential Refractive Index

Typical Gel permeation chromatogram of poly-E-polystyrene (sample G39)
the practical reasons mentioned above.

\( \text{s-BuLi concentrations, with respect to } \text{SBR}, \text{covered a range of values from } 5.9 \text{ to } 32.0 \text{ moles/}10^{-5}\text{ g } \text{SBR. Samples G31 and G32 with values of } 11.5 \text{ and } 32.0 \text{ moles/}10^{-5}\text{ g } \text{SBR, respectively, had very similar grafting efficiencies. Assuming grafting efficiency is independent of } [\text{TMEDA}]/[\text{s-BuLi}] \text{ when the values are large, as suggested in section 4.6.2 for the same metalation system, then for the range of initiator values used grafting efficiency is unaffected by changes in s-BuLi concentration (moles/}10^{-5}\text{ g } \text{SBR). This is as expected because the number of initiating molecules will be very small compared to the number of potential graft sites and therefore will react almost independently of each other. It is only when there is competition for each of the metalatable sites, i.e. at very high complex concentrations, that s-BuLi concentration will affect grafting efficiency.}

It has already been shown in section 4.6.2 that using large values of \([\text{TMEDA}]/[\text{s-BuLi}]\) does not appear to have a detrimental effect on grafting efficiency when cyclohexane is the solvent. The range of values in the present preparations, i.e. 14.0 to 74.0, does not show any distinctive trends with respect to grafting efficiency and therefore the continued use of large amounts of TMEDA to reduce the solution viscosity, enabling better mixing, was not considered detrimental.

The results in table 4.13 show that the only samples with grafting efficiencies below 60% are G30 and G39, which are probably due to the short metalation times employed (\( \leq 5 \text{ hours} \)). This latter sample was metalated at 50°C and although the grafting efficiency value is lower than that obtained for sample G38 prepared under similar conditions the grafting efficiencies for these short metalation periods at elevated temperatures are no better than those for samples metalated for longer periods at room temperature. It will be shown in section 4.7.4 that, in
methylcyclohexane, metalating at elevated temperature does not appear to improve grafting efficiency even over extended periods. In conclusion it can be said that, for the different metalation conditions employed in the present preparations (G30-G39), only reduced metalation times have any adverse effects.

It is interesting to compare these grafting efficiency values with those obtained for the same metalation reactions in cyclohexane for the SBR-g-polystyrene preparations (table 4.11). Values are generally higher for the SBR-g-polystyrene systems, e.g. for metalations carried out for 12 hours or more grafting efficiencies of 90 to 100% are obtained compared to 66 to 82% for the SBR-g-poly(α-methylstyrene) preparations. Possible reasons for this are discussed in section 4.7.4.

Variables which can possibly affect the extent of polymerisation and therefore yield are: initiator and monomer concentrations, polymerisation time and temperature and the amount of THF present. The initial s-BuLi concentration range used for metalation did not appear to affect the yield, as indicated by samples G31 and G32 having similar grafting efficiencies and yields but different initiator concentrations (mentioned earlier), assuming the different [TMEDA]/[s-BuLi] values used, i.e. 37.0 (G31) and 14.0 (G32), are not significant.

No specific preparations were carried out in the present series to study the effects of varying the amount of monomer used, values were kept fairly constant at 46 ± 5% wt. total (SBR + monomer) feed.

Repeating the experimental conditions used for the preparation of poly(α-methylstyrene), sample H9, of -35°C for 5 hours, preliminary grafting experiments gave very poor yields. In an attempt to increase the yield the polymerisations were carried out for periods of up to 21 hours, however, even after these extended periods yields of less than 50% were obtained for polymerisations carried out at -35°C. These low yields
cannot be attributed to equilibrium monomer effects because it has already been shown that homopolymer prepared in this solvent at -35°C can be obtained in yields in excess of 80% (H9, table 4.12). Equilibrium monomer concentration ([H]e) studies of α-methylstyrene in polar (406) and non-polar (228) solvents indicate that [H]e would not account for more than 8% of the total monomer at -35°C. A possible explanation for the poor yields could be a drop in the polymerisation rate as a result of the presence of the high molecular weight SBR material causing an increase in solution viscosity and therefore a reduction in molecular mobility. Attempts were made to follow the kinetics of samples G31 and G32 by measuring sample weight increases, however, because of the small conversions involved the results were subject to considerable errors and were therefore rejected.

In view of the poor yields obtained even after long polymerisation periods at -35°C preparations were carried out at lower temperatures, i.e. -47 (G30) and -78°C (G33, G38 and G39). Considerable improvements in yield were obtained as shown in table 4.13. The polymerisation of α-methylstyrene performed at two temperatures, i.e. -35 (9 hours) and -78°C (10 hours) for sample G33, gave G.P. Mp(obs) values, for samples taken at the end of each of these polymerisation periods, of 32,000 and 46,000, respectively. The increase in yield on going to lower temperature is confirmed when we compare the yield for G33 (80%) with those for samples prepared at -35°C in the presence of a similar amount of THF and for a similar overall polymerisation period, e.g. samples G31 (35%), G32 (32%) and G36 (36%). Possible reasons for an increase in yield at lower temperatures are discussed in section 4.7.4.

The effect of THF content on polymer yield was investigated at -35°C (samples G34-G37), all experimental conditions except for THF content were held constant. The results suggest that yield decreases with THF content, however, other factors may have contributed to give these unexpected
results. It was noticeable that during the THF transfer to samples G35 and G37 the solutions turned a much lighter red, which was then followed by the formation of small amounts of gel material. As much as 10% wt. of the final products of these samples was found to be insoluble when used for g.p.c. analytical purposes. Because there was some uncertainty as to the composition of the insoluble material only approximate grafting efficiency values were obtained. The extremely small amounts of homopolymer produced and the overlap of the g.p.c. peaks meant only \( h_p(\text{obs}) \) values for the poly(\( \alpha \)-methylstyrene) could be determined. Sample G36, which did not appear to contain any insoluble material, also showed considerable overlap of g.p.c. peaks and therefore only an approximate grafting efficiency value could be calculated, similarly only \( h_p(\text{obs}) \) could be obtained for the homopolymer present. The peaks for G34 were, however, resolvable and therefore a more precise value for grafting efficiency could be quoted. Colour fading and gel formation in samples G35 and G37 strongly suggests that partial termination and crosslinking has occurred. There are potentially three sources from which this inactivity can arise, these are: the THF itself, impurities in the THF and impurities introduced during the THF transfer procedure. It is therefore possible that the effects observed in the above samples may also occur in other preparations involving THF, but to a lesser extent. It has already been mentioned that the polydispersities for the homopolymers in samples G35 and G37 could not be obtained, however, even if values were available they would only give an indication of possible termination processes occurring during, rather than before, \( \alpha \)-methylstyrene polymerisation. The polydispersity values for four homopolymer samples present in the graft copolymer products (G30, G34, G38 and G39) are given in table 4.9. Although the values for G30 and G34 are slightly higher than those found for polystyrene homopolymers the differences are not significant enough to suggest that premature termination is occurring during \( \alpha \)-methylstyrene polymerisation.
Comparing the $n_p(\text{obs})$ values with the calculated molecular weight (Y's) values for the homopolymers obtained (table 4.13) we see that there is poor agreement and that the observed values are consistently higher by as much as a factor of 10. Because there is reasonable agreement between $n_p(\text{obs})$ and the calculated molecular weight values for the polystyrene homopolymers (table 4.11), the present results suggest that large amounts of initiator are 'killed off' on THF addition in nearly all the preparations. As a result the $A'$ values for $\text{SBR-g-poly(}\alpha\text{-methylstyrene)}$ are lower than for the $\text{SBR-g-polystyrene}$ systems at similar initiator levels. If termination effects are not wholly responsible for the apparent reduction in the amount of 'active' initiator another possibility is that $A$ and $A'$ (as defined in section 4.5.5) are not the same, i.e. some graft sites are present which initiate styrene polymerisation but do not initiate $\alpha\text{-methylstyrene}$ polymerisation. This may be attributable to steric hindrance effects as a result of the bulky methyl substituent present in $\alpha\text{-methylstyrene}$. For example, if only aromatic metalation positions initiate $\alpha\text{-methylstyrene}$ polymerisation this will not only give a much higher graft molecular weight than anticipated but also increase the amount of material existing as homopolymer, assuming grafting efficiency is not 100%.

4.7.4 Grafting in Methylcyclohexane/THF

In view of the considerable amounts of THF required to prevent cyclohexane from freezing in the previous systems and the possibility of premature termination effects as a result of adding these large amounts of solvent, methylcyclohexane was considered a suitable replacement for cyclohexane because then only sufficient amounts of THF to get a reasonable conversion need be added.

The g.p.c. and yield results for $\text{SBR-g-poly(}\alpha\text{-methylstyrene)}$ samples prepared in methylcyclohexane/THF under various experimental conditions
(see table 3.9) are given in table 4.14. As with the preparations in cyclo-
hexane/THF, SBR concentrations were kept fairly constant throughout, i.e.
1.5 ± 0.3% w/v. Similarly s-BuLi concentrations were kept within the range
13.3 to 20.5 moles/10^5 g SBR to enable comparisons to be made between
different groups of experiments.

Samples G51 and G52 were prepared under identical experimental condi-
tions except for their [TMEDA]/[s-BuLi] values of 0.9 and 3.8, respectively.
Although there appears to be no difference in their grafting efficiency
values, comparing these results with those obtained for samples G40 and
G41 having [TMEDA]/[s-BuLi] values of 26.0 and slightly shorter metatation
times (22.5 hours as opposed to 28.3 hours) we see a considerable drop in
grafting efficiency with these latter samples. The differences cannot be
explained purely in terms of shorter metatation times because other pre-
parations in this group with metatation times of 19 hours or less have
grafting efficiencies above 60% (G42-G50).

It was mentioned in section 4.6.2 that an equilibrium may exist bet-
ween metatated polymer and metatated TMEDA, especially as s-BuLi will
metatate TMEDA much more readily than n-BuLi (239). Adding TMEDA in
excess of the stoichiometric amounts would increase the probability of
TMEDA metatation. It was suggested by Langer (239) that the s-BuLi.metat-
atation of TMEDA forms a bicyclic structure (I) which then combines with
another metatated species to form a less strained ring structure (II) and

\[ \text{(I)} \]

\[ \text{(II)} \]

because it still contains active C-Li species is capable of initiating
polymerisation. The effectiveness of metatated TMEDA (II) as a metatating
<table>
<thead>
<tr>
<th>Sample ref.</th>
<th>Yield (%)</th>
<th>GE (%)</th>
<th>homopolymer M_p(obs) (x 10^{-3})</th>
<th>calc. graft mol. wt. (x 10^{-3})</th>
<th>A'</th>
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</tr>
<tr>
<td>G53</td>
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<td>-</td>
<td>8.5</td>
<td>0.6</td>
<td>-</td>
</tr>
<tr>
<td>G54</td>
<td>10</td>
<td>-</td>
<td>-</td>
<td>0.5</td>
<td>-</td>
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</tbody>
</table>

a) For synthesis details see table 3.9.
agent for backbone polymers such as polybutadiene is, however, questionable.

Preparations in which a $\text{[TMEDA]}/\text{[s-BuLi]}$ ratio of approximately 1 was used (G45, G46 and G51) showed no improvement in grafting efficiency over preparations where $\text{[TMEDA]}/\text{[s-BuLi]}$ values of approximately 6 were employed (G43, G44, G47-G50). Therefore, adding TMEDA in excess of the 1:1 stoichiometric amounts with s-BuLi does not affect grafting efficiency, as found with the SBR-$\alpha$-polystyrene systems (section 4.6.2). For the conditions used (table 3.9) 'excess' TMEDA does not appear to promote the formation of metalated species of the type given above (structures I and II), or if they do form their reactivity towards SBR backbone metalation is not unlike that of the s-BuLi.TMEDA complex.

Up to now our discussion has been based on the fact that the extent of metalation, and therefore grafting efficiency, is fixed prior to the polymerisation period. The grafting efficiencies for the samples prepared in methylcyclohexane/THF (G40-G53) have been plotted against the percentage THF present during polymerisation and are shown in figure 4.29. Grafting efficiencies are generally found in the 60 to 70% range, however if G47 is not an anomalous result and because styrene grafting of SBR in cyclohexane in the absence of THF produces high grafting efficiencies ($\geq 80\%$) it could be argued that in the 0 to 10% vol. THF range efficiency decreases with increasing THF content, above 10% vol. the values remain constant. It has already been suggested (equations (4.31) and (4.32)) that THF can react with various 'living' polymer species to produce inactive products, these reactions did, however, require long reaction times before their effects became noticeable. In the present systems where THF is used as cosolvent, the narrow molecular weight distribution homopolymers obtained (table 4.9) do suggest that if a reaction with THF does take place it must occur prior to $\alpha$-methylstyrene polymerisation, i.e., during the period at room temperature. Two samples, mentioned
FIGURE 4.29
The effect of THF content on grafting efficiency for SBR-g-poly(α-methylstyrene) samples prepared in methylcyclohexane/THF

FIGURE 4.30
The effect of THF content on yield for SBR-g-poly(α-methylstyrene) samples prepared in methylcyclohexane/THF at -78°C for 24 ± 3 hours
earlier, i.e. G40 and G41, with very low grafting efficiencies compared to the other samples (see figure 4.29), differed in their synthesis method from the other preparations in that, prior to immersion into the low temperature baths, the solutions were heated to 50°C for several minutes. To reduce grafting efficiency and reduce the amount of 'active' initiator the results suggest the occurrence of termination and transfer processes which are accelerated on heating. The actual extent of THF involvement is, however, uncertain in view of the narrow band of grafting efficiency values obtained for the majority of the samples. Further discussion on the possible causes of the grafting efficiency and homopolymer molecular weight differences between styrene and \( \alpha \)-methylstyrene graft copolymersystems is given in section 4.8.

Other experimental parameters considered as having a possible effect on grafting efficiency were metatlation time and metatlation temperature. Comparing samples G49 and G52, having similar metatlation conditions except for metatlation times of 19 and 28.3 hours, respectively, no differences in grafting efficiency were found and therefore extending the metatlation period beyond 19 hours does not appear to reduce the amount of 'free' initiator present in the system. Samples G43 and G46 metalated at 50°C for 14.7 and 18.0 hours, respectively, did not show any marked deviations from grafting efficiency values obtained at room temperature, similar results were found with SBR metalations in cyclohexane (section 4.6.2).

To compare yields for the samples prepared (G40-G54), monomer feed was held constant throughout (36 ± 2% wt.). The effect of THF content on yield is shown in figure 4.30 for all SBR-g-poly(\( \alpha \)-methylstyrene) preparations carried out in methylcyclohexane/THF at 78°C for 24 ± 3 hours. Sample G29 in which no THF was used, is given as reference. Samples G47 to G50 were carried out specifically to investigate varying
THF content, all other variables being kept constant. It can be seen from these specific sample results and for the other samples given, that yield increases with THF content for the range covered. Rate studies carried out on several of the polymers are discussed in section 4.7.6.

Two groups of experiments (G52-G54; G43 and G44) were carried out to investigate the effects of polymerisation temperature at THF levels of approximately 27 and 9% vol., respectively. Yield versus polymerisation temperature data are given in figure 4.31. It is apparent that for a fixed polymerisation period yield decreases dramatically with increasing polymerisation temperature. These differences are more than can be accounted for by equilibrium monomer concentration effects, especially for the temperature range covered. It would generally be expected for polymerisation rate to decrease with decreasing temperature and therefore for a system in which polymerisation has not reached completion, yields will be greater for the preparations carried out at higher temperatures, ignoring equilibrium effects. To explain the results in figure 4.31 and similar ones found with the cyclohexane/THF system (section 4.6.2) it is necessary to consider the types of propagating species that could be present. In hydrocarbon solvent organolithium initiated polymeric species exist in associated form whereas in polar solvent associations do not occur (see section 2.1.2). It was anticipated that the presence of TMEDA in the form of a complex with the lithiated SBR 'sites' would prevent 'living' end associations, however, in most cases where TMEDA was not used in excess amounts viscosity increases during metatlation suggested that associations were occurring between 'living' sites. Similar viscosity increases were also noticeable during polymerisation (see section 3.4.3), however, because THF was added in substantial amounts the viscosity changes were probably due to low temperature effects rather than actual chain associations. Therefore it was assumed that, in the presence of THF,
The effect of polymerisation temperature on yield for SBR-g-poly(α-methylstyrene) prepared in methylcyclohexane/THF with THF present as 9% vol. (G43 and G44) and 27% vol. (G52-54) total solvent.

![Graph showing the effect of polymerisation temperature on yield for SBR-g-poly(α-methylstyrene).](image1)

**Figure 4.32**

The effect of THF content on yield for SBR-g-poly(α-methylstyrene) samples prepared in methylcyclohexane/cyclohexane/THF at -40°C for 44 hours.

![Graph showing the effect of THF content on yield.](image2)
polymerisation proceeded via unassociated chain (graft) ends. The chain ends may be in the form of contact ion pairs, solvent (or THEDA) separated ion pairs or free ions. In non-polar solvent it has been suggested that the propagating species are either in the form of contact ion pairs (239) or THEDA separated ion pairs (221). The addition of polar solvent as shown by equation (2.9) will, however, discourage contact ion pair formation. Although the individual rate constants for each of the chain end species may decrease with temperature, the relative amounts of each could also change with temperature. Rate constants increase in the order, contact ion pairs < solvent separated ion pairs < free ions, and as decreasing the temperature favours the formation of larger amounts of the higher rate constant species (39) it is possible that if a composite rate constant dictates the overall polymerisation, rate could increase on lowering the temperature. Therefore, for systems where polymerisation is still continuing the greater yields will be obtained for the systems with the largest rate constants. Further discussion on the kinetics of the systems is given in section 4.7.6.

Although no specific group of experiments was carried out to analyse the effects of polymerisation time, it was found that reasonably high yields could be obtained within 24 hours if the reactions were carried out at -78°C.

In conclusion, it can be said that although considerably smaller amounts of THF were used in the present methylcyclohexane systems compared to that used in the cyclohexane preparations (section 4.7.3), similar grafting efficiencies and molecular weight differences were obtained.
4.7.5 Grafting in Methylcyclohexane/Cyclohexane/THF

Several preparations were carried out in a mixed hydrocarbon/THF system using the experimental conditions given in table 3.10. The yields and the various g.p.c. determinations (as defined in section 4.5) are given in table 4.15. The experiments were divided into two main groups. In the first group (G55 - G58) the effect of THF content on yield at -40°C was investigated. In the second group (G59 and G60) the effect of polymerisation temperature on yield was investigated. THF content versus polymer yield results are given in figure 4.32, sample G56 in which no THF was used is given as reference. The increase in yield with increasing % vol. THF was similar to that found with the methylcyclohexane/THF systems at -78°C (figure 4.30). Therefore to achieve similar yields at a higher temperature, -40°C as opposed to -78°C, for a given THF content, longer polymerisation times must be employed, i.e. approximately twice as long.

The yields for G59 and G60 indicate that for samples prepared under almost identical conditions a larger yield is obtained for the lower temperature preparation, as found with the methylcyclohexane/THF systems (figure 4.31). Rate studies carried out on these two preparations are discussed in section 4.7.6.

Although no particular study was made of metalation conditions in the present polymer systems the differences in experimental conditions for the two groups of experiments carried out (table 3.10) did not produce any large differences in grafting efficiency (73 ± 5%). The calculated and observed molecular weights given in table 4.15 show similar differences to those found with the other α-methylstyrene grafting systems (tables 4.13 and 4.14).

Because of the apparent similarity between the present preparations and the single hydrocarbon/THF systems no further studies were carried out.
### TABLE 4.15

**G.p.c. and Yield Results for SBR-g-poly(α-methylstyrene)**

*prepared in Methylcyclohexane/Cyclohexane/THF*

<table>
<thead>
<tr>
<th>Sample ref.</th>
<th>Yield (%)</th>
<th>GE (%)</th>
<th>homopolymer $M_p$ (obs) (x $10^{-3}$)</th>
<th>calc. graft mol. wt. (x $10^{-3}$)</th>
<th>$A'$</th>
</tr>
</thead>
<tbody>
<tr>
<td>G55</td>
<td>53</td>
<td>70</td>
<td>12.4</td>
<td>2.0</td>
<td>3.2</td>
</tr>
<tr>
<td>G57</td>
<td>62</td>
<td>73</td>
<td>6.1</td>
<td>1.4</td>
<td>4.7</td>
</tr>
<tr>
<td>G58</td>
<td>58</td>
<td>78</td>
<td>9.9</td>
<td>2.4</td>
<td>5.3</td>
</tr>
<tr>
<td>G59</td>
<td>50</td>
<td>68</td>
<td>13.6</td>
<td>1.2</td>
<td>0.9</td>
</tr>
<tr>
<td>G60</td>
<td>65</td>
<td>74</td>
<td>18.4</td>
<td>2.0</td>
<td>1.2</td>
</tr>
</tbody>
</table>

a) For synthesis details see table 3.10.
4.7.6 Kinetics of $\alpha$-methylstyrene Polymerisation

Kinetic studies were carried out to investigate the effects different experimental conditions had on polymerisation rate and to determine whether equilibrium effects were responsible for some of the low yields obtained.

Initial studies were performed on homopolymer systems only (H6-H12). Of the two parameters considered for monitoring the extent of reaction, i.e. $M_n$ (or $M_p(\text{obs})$) and weight of polymer, the latter method was found to be more reliable because values for $M_n^{\infty}$ (see section 4.1.2) could only be determined from the actual amount of initiator added and therefore no allowances were made for termination effects. From the calculated amount of $\alpha$-methylstyrene present in an accurately measured sample and the weight of polymer obtained, it was possible to plot conversion versus time curves, as shown in figures 4.33 to 4.37.

For a reversible anionic polymerisation of the type

$$\begin{align*}
\text{[M]}^\text{Li}^+ + \text{M} & \rightleftharpoons \text{[M]}^{\text{Li}^+} \\
\text{n-mer} & \rightleftharpoons \text{(n+1)-mer}
\end{align*} \tag{4.33}
$$

the rate of polymerisation can be given by a modified form of equation (2.10) (241)

$$\frac{d[M]}{dt} = k_1 ([M] - [M]^*_e) \quad \tag{4.34}$$

where $[M]^*_e$ is the equilibrium monomer concentration (moles l$^{-1}$). For a pseudo first-order reaction with respect to monomer, and taking $[M]^*_o$ to represent the initial monomer concentration, then linear plots of

$$\log \left(\frac{([M]^*_o - [M]^*_e)}{([M] - [M]^*_e)}\right)$$

against time should be obtained. However, a kinetic analysis was first carried out using the poly($\alpha$-methylstyrene) conversion curve values of $x$, the weight fraction of
monomer converted to polymer, to construct \(-\log (1-x)\) against time plots, ignoring equilibrium effects. Taking \((1-x)^{-1}\) to represent \([M]_0/[M]\) the linear traces obtained suggest that, for the temperature range used, values of \([M]_e\) are trivially small and can therefore be ignored. It was mentioned in section 4.7.3 that \([M]_e\) values account for less than 8% of the total monomer at temperatures below -35°C (206), this was further confirmed when conversion versus time curves were extrapolated to values close to the final conversion values and the resulting first-order plots deviated considerably from linear behaviour.

The first-order rate plots given in figures 4.33 and 4.34 for samples prepared in THF (H8) and cyclohexane/THF (H9) do not extrapolate to the origin. It is apparent from their respective conversion curves that high conversion is reached even before samples are extracted. This initial fast polymerisation rate, which is not accounted for by the kinetic data obtained, may occur during the period in which the reactor is cooling to the working temperature. If this is so then the apparent change in polymerisation rate can be attributed to a change in temperature. We would expect this effect to occur in all the preparations, however, at reduced THF levels it appears that the working temperature is reached before any appreciable amounts of polymer form, only sample H10 shows a slight shift along the -log (1-x) axis (figure 4.35).

Samples H11 and H12, given in figures 4.36 and 4.37, show a deviation from first order behaviour as the polymers precipitate from solution. The precipitation points correspond to calculated molecular weights of less than 8,000, therefore to achieve molecular weights much in excess of this value larger quantities of THF (> 10% vol.) would be required.

To compare polymerisation rates in each of the solvent systems used pseudo first-order rate constants, \((k_1)\), were obtained from the slopes of the -log (1-x) versus time plots. Values of \(k_1\) are, however, a function of 'living' polymer concentration and therefore, in view of the differences
Conversion versus time curve and first-order rate plot with respect to monomer consumption for the polymerisation of α-methylstyrene in THF at -40°C (sample H8).
**FIGURE 4.34**

Conversion versus time curve and first-order rate plot with respect to monomer consumption for the polymerisation of \( \alpha \)-methylstyrene in cyclohexane/THF at \(-35^\circ\text{C}\) (sample H9)
Figure 4.35
Conversion versus time curve and first-order rate plot with respect to monomer consumption for the polymerisation of α-methylstyrene in methylcyclohexane/THF at -78°C (sample H10)
FIGURE 4.36
Conversion versus time curve and first-order rate plot with respect to monomer consumption for the polymerisation of α-methylstyrene in methycyclohexane/cyclohexane/THF at -78°C (sample H11)

Point at which precipitate began to appear

Point at which precipitate began to appear
FIGURE 4.37
Conversion versus time curve and first-order rate plot with respect to monomer consumption for the polymerisation of α-methylstyrene in methylcyclohexane/cyclohexane/THF at -78°C (sample H12)
in initiator concentration used, it would be more appropriate to compare apparent bimolecular rate constant (k₂) values. These were obtained by combining equations (2.10) and (2.11) and taking initiator concentration as an approximation of 'living end' concentration. Values of k₁ and k₂, for the various preparations mentioned above, are given in table 4.16. Only approximate comparisons can be made because the k₂ values obtained are based on the assumptions that chain end associations do not occur and that propagation is by one particular species only, i.e., ion pairs. It was mentioned in section 4.7.4 that it is possible for more than one species to be involved in propagation and if free ions are involved then values of k₂ become dependent on 'living end' concentration (see equation (2.17)).

As a result of polymer precipitation the deviation from first order behaviour for sample H12, (figure 4.37), prevented rate constant values being obtained.

Comparing the results for samples H10 and H11, prepared at -78°C, the larger k₂ value obtained for H10 can be attributed to the presence of a larger amount of THF. This can be explained in terms of the increase in solvent polarity encouraging the formation of the highly active free ions (equation (2.9)). It was therefore anticipated that in a pure THF system a large value for k₂ would be obtained. The low value for H9 compared to that for H9 may be attributed to the higher polymerisation temperature used in the latter preparation. Values of k₂ obtained by Worsfold and Bywater (206) for the sodium naphthalene initiated polymerisation of α-methylstyrene in THF were found to decrease with temperature. The possible oversimplified theoretical treatment used for the determination of k₂ values cannot, however, be overlooked, especially when high THF containing systems are involved, where both free ions and ion pairs may contribute to propagation. The change in k₂ with initiator concentration found by the above workers endorses this statement. The k₂ value of
### TABLE 4.16

Rate Constants for α-methylstyrene Polymerisations

<table>
<thead>
<tr>
<th>Sample ref. (^{a})</th>
<th>Polymerisation temp. (°C)</th>
<th>THF present as solvent (% vol.)</th>
<th>s-BuLi (m moles (1^{-1}))</th>
<th>(k_1 \times 10^3) (min (^{-1}))</th>
<th>(k_2) (1 mole (^{-1}) min (^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>H8</td>
<td>-45</td>
<td>100.0</td>
<td>5.7</td>
<td>3.0</td>
<td>0.5</td>
</tr>
<tr>
<td>H9</td>
<td>-35</td>
<td>59.0</td>
<td>3.1</td>
<td>3.7</td>
<td>1.2</td>
</tr>
<tr>
<td>H10</td>
<td>-78</td>
<td>24.6</td>
<td>2.4</td>
<td>1.7</td>
<td>0.7</td>
</tr>
<tr>
<td>H11</td>
<td>-78</td>
<td>4.5</td>
<td>0.8</td>
<td>0.3</td>
<td>0.4</td>
</tr>
<tr>
<td>G42</td>
<td>-78</td>
<td>43.8</td>
<td>1.3</td>
<td>2.2</td>
<td>1.7</td>
</tr>
<tr>
<td>G43</td>
<td>-78</td>
<td>9.1</td>
<td>1.9</td>
<td>0.6</td>
<td>0.3</td>
</tr>
<tr>
<td>G50</td>
<td>-78</td>
<td>38.8</td>
<td>2.0</td>
<td>2.0</td>
<td>1.0</td>
</tr>
<tr>
<td>G59</td>
<td>-40</td>
<td>9.5</td>
<td>2.0</td>
<td>0.4</td>
<td>0.2</td>
</tr>
<tr>
<td>G60</td>
<td>-78</td>
<td>9.1</td>
<td>1.9</td>
<td>0.6</td>
<td>0.3</td>
</tr>
</tbody>
</table>

\(^{a}\) For full synthesis details see tables 3.4 (H8-H11), 3.9 (G42, G43, G50) and 3.10 (G59, G60).
0.5 l mole\(^{-1}\) min\(^{-1}\) obtained for sample H3, prepared in a pure THF system at \(-45^\circ\)C in the presence of s-BuLi only, is considerably less than the value obtained for the sodium naphthalene initiated system (206) at this temperature (\(k_2 = 60\) l mole\(^{-1}\) min\(^{-1}\)).

Considering sample H9, prepared in a mixed solvent system in the absence of TMEDA, the relatively high \(k_2\) value and the high yield suggests that \(\alpha\)-methylstyrene grafting reactions, if carried out at this temperature (\(-35^\circ\)C), will produce high yield products. However, in all grafting preparations at this temperature, yields were low even after extended polymerisation periods. The small conversions in this solvent system (section 4.7.3), as mentioned earlier, prevented any kinetic data being obtained. The yields do suggest, however, that TMEDA has an adverse effect on the kinetics of the system.

Conversion versus polymerisation time data were obtained for several \(\alpha\)-methylstyrene grafting systems (figures 4.38-4.40). Plots of -log (1-x) against time gave a first-order rate, with respect to monomer, for all the samples measured. Rate constants for each are given in table 4.16. The results show that at constant temperature (\(-78^\circ\)C) rate increases with THF content and at a constant THF level (9% vol.) the rate increases with a reduction in temperature. This is consistent with the yield results discussed in sections 4.7.3, 4.7.4 and 4.7.5. The \(k_2\) results are also in reasonable agreement with homopolymer values obtained for the preparations in which TMEDA was present.

The apparent complexity of the TMEDA containing systems is reflected in the increase in polymerisation rate on going to lower temperatures, which strongly suggests that several different species are involved in propagation, as mentioned in section 4.7.4.

Although values of \(k_2\) may be in error as a result of the method used for their determination, as indicated by the lack of agreement with the
Conversion versus time curve and first-order rate plot with respect to \( \alpha \)-methylstyrene consumption for the preparation of SBR-\( g \)-poly(\( \alpha \)-methylstyrene) in methylcyclohexane/THF at \(-78^\circ\text{C}\) (sample G50)
Conversion versus time curve and first-order rate plot with respect to \( \alpha \)-methylstyrene consumption for the preparation of SBR-g-poly(\( \alpha \)-methylstyrene) in methylcyclohexane/THF at \(-78^\circ C\) (samples G42 and G43).
Conversion versus time curve and first-order rate plot with respect to α-methylstyrene consumption for the preparation of SBR-g-poly(α-methylstyrene) in methylcyclohexane/cyclohexane/THF at -40°C (sample G59) and -78°C (sample G60).
Worsfold and Bywater results (206), the present studies were, however, undertaken primarily to establish whether the low yields obtained in some preparations were due to equilibrium rather than kinetic effects and as sufficient information has been obtained to strongly suggest the latter, no further investigations were carried out.
4.8 **SBR-g-POLY(α-METHYLSTYRENE-co-STYRENE)**

It was mentioned in sections 4.7.3 and 4.7.4 that the differences in grafting efficiencies between SBR-g-polystyrene and SBR-g-poly(α-methylstyrene) systems could be due either to the presence of THF or as a result of steric hindrance effects in the latter preparations. In an attempt to establish which of these effects was primarily responsible, several SBR graft copolymers were prepared in which the monomer used was a mixture of α-methylstyrene and styrene. Studies of the anionic copolymerisation of styrene and α-methylstyrene in THF at 25°C (44) and -78°C (242) have shown that styrene polymerises first with the near exclusion of α-methylstyrene, therefore for a mixture of these monomers the resulting polymer will be primarily a polystyrene-poly(α-methylstyrene) AB block copolymer. Referring to section 2.1.5 and taking subscript 2 to represent α-methylstyrene, large values for \( k_{11} \) and \( k_{21} \) compared to \( k_{22} \) and \( k_{12} \) have been attributed to steric hindrance effects as a result of the bulky methyl substituent (44). Preferential polymerisation of styrene in the present studies was not, however, taken for granted especially as the experimental conditions employed were not identical to those used in the above mentioned preparations. The use of \(-co-\) in the nomenclature, as stated in the appendix, serves only to describe a copolymer of the two components and does not differentiate between a random and block copolymer. Graft copolymer preparations were attempted in solvent systems, with and without THF present.

4.8.1 **Grafting in the absence of THF**

G.p.c. and yield results for the samples prepared in methylcyclohexane (G61) and methylcyclohexane/cyclohexane (G62 and G63) are given in table 4.17. Comparing the low yields obtained with the actual amounts of styrene in the monomer feed (see table 3.12) suggests that the poly-
<table>
<thead>
<tr>
<th>Sample ref.</th>
<th>Yield (%)</th>
<th>GE (%)</th>
<th>homopolymer $M_p$ (obs) ($\times 10^{-3}$)</th>
<th>calc. graft mol. wt. ($\times 10^{-3}$)</th>
<th>$A'$</th>
</tr>
</thead>
<tbody>
<tr>
<td>G61</td>
<td>21</td>
<td>63</td>
<td>3.7</td>
<td>2.7</td>
<td>8.6</td>
</tr>
<tr>
<td>G62</td>
<td>8</td>
<td>-</td>
<td>-</td>
<td>0.5</td>
<td>-</td>
</tr>
<tr>
<td>G63</td>
<td>27</td>
<td>87</td>
<td>2.7</td>
<td>1.8</td>
<td>13.8$^b$</td>
</tr>
<tr>
<td>G64</td>
<td>55</td>
<td>$\sim$100</td>
<td>-</td>
<td>3.5</td>
<td>(9.2)</td>
</tr>
<tr>
<td>G65</td>
<td>73</td>
<td>82</td>
<td>4.5</td>
<td>3.7</td>
<td>6.2</td>
</tr>
<tr>
<td>G66</td>
<td>78</td>
<td>94</td>
<td>5.5</td>
<td>4.2</td>
<td>6.6</td>
</tr>
<tr>
<td>G67</td>
<td>49</td>
<td>$\sim$100</td>
<td>-</td>
<td>9.4</td>
<td>(9.5)</td>
</tr>
<tr>
<td>G68</td>
<td>91</td>
<td>85</td>
<td>14.0</td>
<td>8.6</td>
<td>7.2</td>
</tr>
<tr>
<td>G69</td>
<td>50</td>
<td>79</td>
<td>15.2</td>
<td>2.3</td>
<td>1.9</td>
</tr>
<tr>
<td>G70</td>
<td>96</td>
<td>71</td>
<td>9.2</td>
<td>7.0</td>
<td>9.0$^b$</td>
</tr>
</tbody>
</table>

Values in ( ) are for the average number of graft sites per chain ($A'$) as given in table 4.11.

a) For synthesis details see tables 3.11 (G64-G68) and 3.12 (G61-G63, G69, G70).

b) Based on the total, rather than active, amount of initiator.
merised product is mostly composed of styrene. G.p.c. traces of samples taken at the end of each temperature period showed only slight increases in homopolymer $M_p$(obs) values for G61 and G63. The grafting efficiency of sample G62 could not be determined because of the small yield involved, however, the values that were obtained did not indicate any particular trends. The homopolymer $M_p$(obs) values for samples G61 and G63 were found to be in reasonable agreement with the calculated values, as found with the 3BR-g-polystyrene copolymers prepared in cyclohexane (table 4.11).

4.8.2 Grafting in the Presence of THF

G.p.c. and yield results for samples prepared in cyclohexane/THF (G64- G68), methylcyclohexane/THF (G69) and methylcyclohexane/cyclohexane/THF (G70) are given in table 4.16. Considering the cyclohexane/THF preparations first, samples G64, G65 and G66 were polymerised at room temperature for several hours prior to THF addition (see table 3.11). G.p.c. traces for samples taken at the end of room temperature polymerisation indicated that very small amounts of homopolymer were present. After 3.5 hours at $-35^\circ$C and in the presence of THF the g.p.c. trace of G65 showed a well defined homopolymer peak, on lowering to $-78^\circ$C and polymerising for a further 13 hours the homopolymer $M_p$(obs) value increased from 2400 to 4500. Similar changes were observed with sample G66. Comparing the yields for G64, G65 and G66 we see that the value for G64 is lower than the other two samples, probably as a result of polymerisation being carried out at $-35^\circ$C and not $-78^\circ$C. From the % monomer feed values given in table 3.11 it is apparent that polymerisation of $\alpha$-methylstryene has occurred. The grafting efficiency values for the samples are all above 80% and there is reasonable agreement between calculated and observed homopolymer molecular weights. Samples G67 and G68, where THF was added immediately after monomer addition and then polymerisation carried out at sub-zero tempera-
tures, also gave high grafting efficiency values similar to those found above.

Sample G69 prepared in methylcyclohexane/THF and sample G70 prepared in methylcyclohexane/cyclohexane/THF gave rather lower grafting efficiency values, however the latter sample showed that there was good agreement between calculated and observed homopolymer molecular weight values.

In summary, therefore, it would appear that only styrene will polymerise in the absence of THF, producing high grafting efficiency products and homopolymers with molecular weights in reasonable agreement with the calculated values, as found in section 4.6.2. Similar results are, however, obtained for \( \alpha \)-methylstyrene grafting in the presence of THF when styrene is added as part of the monomer feed. The results tend to suggest that styrene polymerises preferentially, with the \( \alpha \)-methylstyrene adding on to the styrene chains. In several preparations quite large amounts of THF were used and therefore if THF was the cause of the large reduction in active initiator and reduction in grafting efficiency, as mentioned earlier (section 4.7.4), the presence of styrene would appear to eliminate these effects. It seems, however, more plausible to explain the present results in terms of steric effects. The inability of \( \alpha \)-methylstyrene to initiate from a proportion of backbone sites would not affect the results because the presence of styrene would enable all sites to initiate polymerisation via this monomer.

Some results (G68 and G69) did show significant differences between calculated and observed molecular weight values, which does indicate that additions of relatively large amounts of solvent to an already initiated system will always cause some degree of termination, regardless of possible solvent-living polymer interactions.
4.9 POLY(VINYLTOluENE) AND SBR-g-POLY(VINYLTOluENE)

Only a small number of preparations were attempted because poly-
(vinyltoluene) was not considered a suitable grafting polymer as a result
of its unfavourable $T_g$ (see table 4.21).

4.9.1 Homopolymer Study

Poly(vinyltoluene) prepared in THF using s-BuLi as initiator (table
3.3) was obtained in greater than 95% yield. G.p.c. traces taken after
1.5 and 16.2 hours polymerisation were identical. The apparent rapid
polymerisation rate, similar to that found with polystyrene and poly-
($\alpha$-methylstyrene) in a pure THF system, was reflected in the large poly-
dispersity value obtained, $M_w/M_n = 1.53$ (taking the polystyrene equivalents
as being good approximations of true values). The $M_n$ value of 15,000 was
close to the calculated value of 12,000 which suggests that only a small
amount of the initiator was deactivated during polymerisation. The homo-
polymer was primarily prepared for $T_g$ determination (see section 4.12).

4.9.2 Grafting in Cyclohexane

Using the experimental conditions given in table 3.13 no detectable
amounts of polymerised vinyltoluene were obtained when THF was the solvent
(sample G71), as found with styrene and $\alpha$-methylstyrene SBR grafting in
this solvent.

The preparation in cyclohexane was performed over an extended poly-
merisation period of 72 hours at 20°C. Product was obtained in high yield
(> 95%) and with a grafting efficiency of approximately 95%. The homo-
polymer, just visible in the g.p.c. trace of the product, having an
$M_p(\text{obs}) = 7700$, compared favourably with the calculated molecular weight
value of 11,000. Therefore allowing for a small amount of impurity
deactivation of initiator, the results are similar to those found for the SBR-g-polystyrene systems in cyclohexane (section 4.6.2). The similarity between styrene and vinyltoluene implies that the presence of a methyl group in the aromatic ring does not affect the ability of the monomer to polymerise from all or nearly all the graft sites.
4.10 CHARACTERISATION OF SBR GRAFT COPOLYMERS

To characterise the graft copolymers it was first necessary to extract any homopolymer present as the result of inefficient grafting. This was achieved using a solvent extraction process. The samples were dissolved in methylcyclohexane and then acetone gradually added until a precipitate formed. The precipitate was found to contain very little homopolymer and by repeating the procedure several times complete removal of homopolymer could be achieved, see figure 4.41. By increasing the initial solution concentration and collecting only the precipitate which appeared first, a single stage process was often all that was necessary to remove all the homopolymer present. The method applied equally to systems containing polystyrene or poly(α-methylstyrene).

4.10.1 Graft Copolymer Composition

The compositions of several SBR graft copolymers were determined by $^1$H NMR using the method described in section 4.4.1. There was no discrimination between styrene and α-methylstyrene and therefore to determine the amount of grafted material present (styrene or α-methylstyrene) it was first necessary to make an allowance for the styrene already present in SBR, this was taken as 24.3% wt. (sample M3, table 4.8). The results for several determinations are given in table 4.18, together with the calculated amounts of graft material determined from grafting efficiency data (method (a), section 4.5.2). The results show that there is reasonable agreement between the two methods. The relative amounts of 1,2 and 1,4-butadiene addition units present should remain constant throughout, however, there are some slight differences but which can be attributed to inaccuracies in measuring the integrated intensities due to NMR peak overlap (peaks K and L in table 4.7), rather than to real effects. The overall butadiene composition remained constant throughout and therefore did not affect the determination of styrene/α-methylstyrene.
SBA-α-POLY(α-METHYLSTYRENE) (G38)

(a) original trace  
(b) after one extraction  
(c) after two extractions  
(d) after three extractions

FIGURE 4.41
Gel permeation chromatograms of SBA-α-POLY(α-METHYLSTYRENE) (sample G38)
before (a) and after (b, c and d) a solvent extraction procedure was used to remove homopolymer

Differential Refractive Index

Counts
### TABLE 4.18

**SBR Graft Copolymer Composition**

<table>
<thead>
<tr>
<th>Sample ref.</th>
<th>Copolymer type</th>
<th>Composition (% wt.)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>1,2-butadiene units</td>
</tr>
<tr>
<td>G19</td>
<td>SBR-g-Ps&lt;sup&gt;b&lt;/sup&gt;</td>
<td>15.7</td>
</tr>
<tr>
<td>G34</td>
<td>SBR-g-PMS&lt;sup&gt;c&lt;/sup&gt;</td>
<td>20.7</td>
</tr>
<tr>
<td>G39</td>
<td>SBR-g-PMS</td>
<td>21.7</td>
</tr>
<tr>
<td>G42</td>
<td>SBR-g-PMS</td>
<td>16.7</td>
</tr>
<tr>
<td>G46</td>
<td>SBR-g-PMS</td>
<td>18.6</td>
</tr>
<tr>
<td>G58</td>
<td>SBR-g-PMS</td>
<td>19.5</td>
</tr>
<tr>
<td>G49</td>
<td>SBR-g-PMS</td>
<td>18.8</td>
</tr>
<tr>
<td>G50</td>
<td>SBR-g-PMS</td>
<td>21.2</td>
</tr>
</tbody>
</table>

---

a) Determined in the absence of homopolymer.

b) SBR-g-polystyrene.

c) SBR-g-poly(α-methylstyrene).
content. The amount of grafted material was taken to be the 'hard' phase content of the polymer (the styrene present in the SBR was regarded as part of the 'soft' (rubber) phase).

4.10.2 Graft Molecular Weight

To compare the graft molecular weight with that of the homopolymer, ozonolysis techniques were required (section 3.7). As mentioned in section 2.5, ozone readily attacks unsaturated groups such as double bonds and if carried out under suitable conditions, can actually cleave the molecule at the point of unsaturation. In the present work the experimental conditions were chosen such that ozone attack would occur at the sites of unsaturation in the SBR backbone, producing ozonides which would then be reduced to carbonyl compounds when triphenylphosphine was added (equation (2.66)). It was hoped that the low temperatures employed would prevent any degradation of the grafted polymer. The products obtained from ozonolysis were analysed by g.p.c. A typical trace is given in figure 4.42, together with the trace of the graft copolymer prior to ozonolysis and the graft copolymer with the homopolymer still present. The ozonolysis product shows a clear peak in the homopolymer position which corresponds to the grafting polymer. There is also a broad peak in the very low molecular weight region which overlaps with the TPE peak. The peak beyond that of TPE corresponds to fragments with molecular weights so small that very little separation occurs and they elute almost together. To confirm that the peak in the 74 to 84% TPE path length range was not due to species already present in the SBR, ozonolysis was carried out on untreated SBR. The g.p.c. trace of the product showed no polymeric species to be present below 90% TPE path length, i.e. having an $M_p(\text{obs})$ value of 1500 or above and as most of the material eluted after TPE it was apparent that the polymeric fragments were composed of only a few monomer units. Because styrene and 1,2-butadiene units do not contain
FIGURE 4.42
Gel permeation chromatograms of SBH-g-poly(o-methylstyrene) (sample G42) initially (A), after homopolymer removal (B) and after ozonolysis of the homopolymer free sample (C)
unsaturated groups in their backbone sections, it is unlikely that blocks of these monomer types are present in any appreciable amounts in view of the low molecular weight fragments obtained, therefore the SBR used (Solyrene 1204) can be regarded as a completely random copolymer of styrene and butadiene.

The g.p.c. results for several grafting polymers, isolated by ozonolysis methods, are given in table 4.19, together with the g.p.c. molecular weight characteristics of their corresponding homopolymers. There is good agreement between graft and homopolymer molecular weights. The increases in polydispersity are probably due to the presence of varying length backbone fragments attached to the polymer grafts, as evidenced by the high molecular 'tails' found in nearly all their g.p.c. traces. It can be seen from the results that homopolymer molecular weight can be satisfactorily represented by $M_p(\text{obs})$ and that this is a good approximation of the true graft molecular weight when the polydispersity values are low. The results also suggest that the propagation species attached to the backbone polymers and those free in the solution have very similar rate constants and can, therefore, be regarded as being identical species.

4.10.3 Graft Copolymer Molecular Weight

Following the methods described in section 3.6, high speed membrane osmometry was used for the determination of $\bar{M}_n$ values for several SBR graft copolymers. The results are given in table 4.20, $\bar{M}_n^*$ and polydispersity values obtained by g.p.c. are included. The results for a sample in which metatation was carried out but was then terminated prior to grafting, sample M3, are included for comparison. Except for sample G16 the graft copolymers all show an increase in $\bar{M}_n$ with respect to the 'starting material', sample M3, which is as expected when grafting occurs. A major problem encountered when measuring $\bar{M}_n$ is highlighted by sample G16.


**TABLE 4.19**

G.p.c. Molecular Weight Results for Grafting Polymer and Homopolymer

<table>
<thead>
<tr>
<th>Sample ref.</th>
<th>Copolymer type</th>
<th>Grafting polymer</th>
<th>Homopolymer</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$\bar{M}_n \times 10^{-3}$</td>
<td>$\bar{M}_p(\text{obs}) \times 10^{-3}$</td>
</tr>
<tr>
<td>G19</td>
<td>SBR-$\varepsilon$-PS</td>
<td>9.2</td>
<td>9.2</td>
</tr>
<tr>
<td>G34</td>
<td>SBR-$\varepsilon$-PMS</td>
<td>18.2</td>
<td>16.7</td>
</tr>
<tr>
<td>G42</td>
<td>SBR-$\varepsilon$-PMS</td>
<td>11.7</td>
<td>12.4</td>
</tr>
<tr>
<td>G46</td>
<td>SBR-$\varepsilon$-PMS</td>
<td>15.1</td>
<td>19.1</td>
</tr>
<tr>
<td>G49</td>
<td>SBR-$\varepsilon$-PMS</td>
<td>11.5</td>
<td>11.7</td>
</tr>
</tbody>
</table>

a) Abbreviations as for table 4.18.
TABLE 4.20
Molecular Weight Characteristics of SBR Graft Copolymers

<table>
<thead>
<tr>
<th>Sample ref.</th>
<th>Copolymer type</th>
<th>$\bar{M}_n$ (x 10^-3)</th>
<th>$\bar{M}_n^*$ (x 10^-3)</th>
<th>$\bar{M}_w^<em>/\bar{M}_n^</em>$</th>
<th>graft mol. wt. (x 10^-3)</th>
<th>$A'$</th>
<th>calc. graft copolymer mol. wt. (x 10^-3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>K3</td>
<td>SBR</td>
<td>117.0</td>
<td>159.0</td>
<td>1.50</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>G16</td>
<td>SBR-g-PS</td>
<td>67.0</td>
<td>162.0</td>
<td>1.61</td>
<td>3.6</td>
<td>17.7</td>
<td>179.0</td>
</tr>
<tr>
<td>G39</td>
<td>SBR-g-PMS</td>
<td>157.0</td>
<td>233.0</td>
<td>1.78</td>
<td>22.0</td>
<td>1.5</td>
<td>151.0</td>
</tr>
<tr>
<td>G49</td>
<td>SBR-g-PMS</td>
<td>144.0</td>
<td>170.0</td>
<td>1.59</td>
<td>10.7</td>
<td>2.6</td>
<td>146.0</td>
</tr>
<tr>
<td>G67</td>
<td>SBR-g-P(MS-co-S)</td>
<td>138.0</td>
<td>200.0</td>
<td>1.56</td>
<td>4.0^f</td>
<td>4.6^e</td>
<td>155.0</td>
</tr>
</tbody>
</table>

a) Determined in the absence of homopolymer, except for sample G16.
b) Nomenclature as in table 4.18.
c) SBR-g-poly(α-methylstyrene-co-styrene).
d) Taken as homopolymer $M_p$(obs)^t.
e) $117,000 + (M_p$(obs) x $A'$).
f) Based on $Y_M$s (see section 4.5.4).
for which a very low \( \bar{M}_n \) value was obtained. Because only a very small amount of homopolymer was present in the final product, no homopolymer extraction process was used, and therefore the \( \bar{M}_n \) of the graft copolymer was measured in the presence of homopolymer. It can be seen from the very low \( \bar{M}_n \) value that its presence has a considerable effect. The sensitivity of \( \bar{M}_n \) to low molecular weight species can be demonstrated by the calculation of the composite number average molecular weight of a two component system (\( \bar{M}_{n12} \)) using the equation (243)

\[
\frac{1}{\bar{M}_{n12}} = \frac{w_1}{\bar{M}_{n1}} + \frac{w_2}{\bar{M}_{n2}}
\]  

(4.35)

where \( w_1 \) and \( w_2 \) are the weight fractions of components 1 and 2. Taking 1 to represent the graft copolymer and 2 to represent the homopolymer in sample G16 and using values of \( \bar{M}_{n12} = 67,000, \bar{M}_{n2} = 4,000, w_1 = 0.965 \) and \( w_2 = 0.035 \) as found, we obtain a value for the graft copolymer molecular weight (\( \bar{M}_{n1} \)) of 156,000. Therefore the presence of homopolymer even in very small amounts (<4% wt.) can drastically reduce \( \bar{M}_n \). Emphasis must therefore be placed on the homopolymer extraction process to ensure that none is present. For all the other samples measured the g.p.c. traces were absent of homopolymer.

Also given in table 4.20 are the theoretical molecular weight values for each sample, calculated from the amount of grafted material present in the copolymer and taking the ungrafted polymer to have a \( \bar{M}_n = 117,000 \) (see later). Also given in table 4.20 are the average number of grafts per chain (\( A' \)), determined as shown in section 4.5.5. The product of homopolymer molecular weight and average number of grafts gives the increase in molecular weight on grafting. Samples G39 and G49 show remarkably good agreement between the calculated and actual graft copolymer \( \bar{M}_n \) values. This suggests that homopolymer 'contamination' does not occur,
however the lower than calculated $\tilde{M}_n$ value obtained by osmometry for sample G93 could be due to the presence of a small amount of homopolymer, which was too small to be detected by g.p.c. at the sensitivities used.

The $\tilde{M}_n$ values determined from g.p.c. data were, in each case, larger than the actual values. An attempt to correlate these discrepancies with differences in calibration data for styrene and butadiene will not be made because of the complexity of the system. It was mentioned in section 2.4.3 that hydrodynamic volume will change considerably with the degree of grafting and as we are dealing with polymers where the number and length of the grafts differ, no true comparisons can be made with any degree of accuracy. Similarly for polydispersity values, although they do appear to increase slightly on grafting as expected (see section 2.3.2), these values are based on linear polymers and therefore cannot be taken as true values. The reason why these approximate polydispersity values were determined was primarily to check for possible effects of backbone degradation by initiator. It was shown earlier (section 4.4.2) that the metalation of SBR in THF produced a relatively narrow distribution polymer almost identical to that of the starting material in the absence of any star copolymer material, whereas in cyclohexane (and presumably in the other hydrocarbon solvents) a small amount of backbone degradation in addition to metalation was apparent. Using large amounts of metalation complex produced considerable broadening in molecular weight distribution and lowering of $\tilde{M}_n$ (sample M4, table 4.6). It could therefore be argued that because of the reduced levels of initiator used, the increases in $\tilde{M}_n$, with respect to sample M3, are not due to grafting but to a reduction in the extent of backbone degradation. Indeed, the samples prepared in THF which do not show signs of degradation do have relatively high molecular weight values. However, for the range of initiator levels used there does not appear to be any correlation between $s$-BuLi concentration and
the $M_n$ and $M_w/M_n$ values obtained, therefore the problem of possible back-
bone degradation is not as extensive as first thought (section 4.4.1).

G.p.c. traces obtained for nearly all SBR metalations prior to monomer 
addition, gave almost identical low molecular weight 'tails' to that of 
sample M3, which tends to suggest that for the narrow range of initiator 
concentrations employed, the degradation effects are almost constant.

Therefore, taking the molecular weight ($M_n$) of SBR as 117,000 and the 
total graft molecular weight as, homopolymer $M_p(\text{obs}) \times A'$, the sum of these 
two values is then a good approximation of the true SBR graft copolymer 
molecular weight.
SECTIOH B: MECHANICAL PROPERTIES

4.11 INTRODUCTION

The properties of a polymeric material will be determined by its chemical composition and structure and also by its morphology, therefore, in any property evaluation each of these must be considered.

In the present work the hard phase content, taken as the amount of vinyl aromatic material polymerised, was kept between 20 and 40% wt. total polymer. This range was chosen because outside these limits ABA (4) and BgA (18) copolymers of styrene and butadiene are considered to have poor elastomeric properties.

With regard to chemical structure, in the case of the SBr graft copolymers, the predominant variables will be the number and length of the grafts. For a fixed composition, the larger the number of grafts, the smaller the graft molecular weight and vice versa. Having a large number of grafts per chain will reduce the amount of 'loose end' backbone material which does not contribute to the reinforcement of the two phase structure and can be regarded as AB block copolymer material which generally has poor elastomeric properties (186). A small number of grafts per chain will mean a bigger graft molecular weight and also a larger backbone molecular weight between grafts, these together with the reduction in the number of chemical linkages between backbone and grafting material favour greater phase separation, as mentioned in section 2.7. The 'ideal' number of grafts per chain is therefore based on a compromise between these various effects. Work carried out by Falk et al. (18) on the styrene grafting of polybutadiene (molecular weight 120,000) indicated that for a styrene content of between 25 and 42% wt. good tensile properties could be achieved for materials containing approximately 5 to 20 grafts per chain. This suggests that phase separation can occur in these graft copolymers when the graft molecular weights are as low as 3000.
Taking the above grafting levels as a guideline, initiator concentrations in the present work were chosen to produce an average number of grafts per chain within this range (see tables 4.11 and 4.17). To enable comparisons to be made of the different synthesis conditions for the various SBR systems, initiator levels were kept fairly constant throughout, however, the apparent reduction in the amounts of effective initiator found with the α-methylstyrene only grafting systems often meant that a small number of grafts with relatively high molecular weights were obtained (see tables 4.13-4.15).

Another problem arising from the graft copolymer preparations is the presence of homopolymer, produced as the result of inefficient grafting and therefore considered as a polymeric impurity. Work carried out by Horton and coworkers (77) on the effects of polystyrene additions to styrene-isoprene-styrene block copolymer systems, indicated that provided the molecular weights of the block polystyrene and homopolymer were similar, the addition of homopolymer, by solution blending, did not have any detrimental effects on tensile properties. An actual increase in tensile strength on homopolymer addition indicated that the polystyrene actually entered the polystyrene domains of the block copolymers, effectively increasing the hard phase content of the block copolymer. In the present SBR systems the apparent similarity between the graft and homopolymer molecular weights (see section 4.10.2) suggested that the presence of homopolymer would not have any adverse effects on the mechanical properties and therefore no homopolymer extraction procedures were carried out.

Although narrow molecular weight distribution grafts and homopolymers were produced as a result of the polymerisation technique employed and were found useful for characterisation purposes, it was not considered essential that narrow distribution polymers were necessary to achieve good mechanical properties.
As mentioned earlier morphology also plays an important role in determining the properties of a polymer and therefore before we can discuss the results of the various tests carried out it is necessary to know something about the solid state morphology of the systems. This can be achieved using differential scanning calorimetry (DSC) and dynamic mechanical thermal analysis (DMTA) techniques which reveal the nature of the phases through the $T_g$ locations and the coupling between the phases through the relaxation strengths. In principle techniques such as SAXS and electron microscopy can also be used but the present systems were not sufficiently ordered to be studied usefully by these methods. The transparency of the moulded and solvent cast samples did, however, indicate that microphase separation was occurring, and that the domains were small compared to the wavelength of light, see section 2.7.
4.12 GLASS TRANSITIONS OF THE MAJOR PHASES

The thermoplastic elastomeric properties of a block copolymer are dependent on the mutual incompatibility of component hard and soft blocks, as mentioned for the styrene-butadiene-styrene ABA block copolymer systems (section 2.7). Information on $T_g$ can tell us something about the extent of phase separation. Considering the graft copolymers prepared in the present work, $T_g$ values obtained by DSC for some of the individual components are given in table 4.21.

<table>
<thead>
<tr>
<th>Sample ref.</th>
<th>Polymer type</th>
<th>$T_g$ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>G9</td>
<td>Polyisoprene</td>
<td>-77</td>
</tr>
<tr>
<td>Solprene 1204</td>
<td>SBR</td>
<td>-56</td>
</tr>
<tr>
<td>H4</td>
<td>Polystyrene</td>
<td>101</td>
</tr>
<tr>
<td>H9</td>
<td>Poly(α-methylstyrene)</td>
<td>164</td>
</tr>
<tr>
<td>H13</td>
<td>Poly(vinyltoluene)</td>
<td>85</td>
</tr>
</tbody>
</table>

a) Sample obtained prior to grafting.

The high $T_g$ of SBR relative to polyisoprene can be explained in terms of a composite $T_g$ for the three components present, i.e., butadiene 1,2 and 1,4 addition units and styrene, having $T_g$ values of -30, -90 and 100°C respectively (156). Using the weight fraction results obtained by NMR (table 4.8) and modifying equation (2.89) to include a third component, the composite $T_g$ for SBR is -58°C, which is very close to the actual value obtained. For an ideal block copolymer phase separated system, figure 2.11(IV), it can be seen that suitable modulus values are only
obtained between the glass transitions of the two phases, therefore, for a thermoplastic elastomer to have good physical properties over a wide temperature range it is necessary to have hard and soft phases with vastly different values of $T_g$. For most practical purposes polystyrene is a suitable hard phase, however, in applications where it is desirable to use the material at temperatures of 80°C or above a polymer with a $T_g$ higher than 100°C is required. Two possibilities were considered; poly($\alpha$-methylstyrene) and poly(vinyltoluene). The $T_g$ for poly($\alpha$-methylstyrene) was found to be 164°C (sample H9). As mentioned earlier, vinyltoluene is the collective trivial name for the ortho, meta and para isomers of methylstyrene. Polymers of each of these isomers have $T_g$s of 120, 77 and 101°C respectively (156). Vinyltoluene is, however, only commercially available as a mixture of meta (40%) and para (60%) isomers and applying equation (2.89) this gives a composite $T_g$ of 86°C. The actual value obtained for sample H13 was 85°C. Using this vinyltoluene mixture would not therefore be an improvement over a styrene system. The only isomer of interest (ortho) was cost prohibitive and therefore no further work was carried out with this particular group of monomers.

Polystyrene and poly($\alpha$-methylstyrene) in the form of AB and ABA block copolymers or as a blend show considerable compatibility up to high molecular weight, as evidenced by the single $T_g$ values obtained by various workers (244, 245). A combination of the two monomers either as a random or a block copolymer can be used as a single hard phase component with a $T_g$ dependent on the relative amounts of each monomer present. It was found (245) that an ABA block copolymer of the two monomers did have a single $T_g$ between that of the individual components, but was slightly higher than that calculated for a random copolymer of the same composition. The high $T_g$ and cost of $\alpha$-methylstyrene does suggest that a proportion of the $\alpha$-methylstyrene could usefully be replaced with the less expensive styrene monomer and still produce a hard phase with a favourable $T_g$. 
Although no copolymers of styrene and \( \alpha \)-methylstyrene only were prepared, mixtures of these monomers were used to graft SBR (section 3.4.4).

It was mentioned in section 2.6.4 that \( T_g \) is dependent on molecular weight and as shown by equation (2.90) will decrease with decreasing molecular weight. \( K \) values of approximately \( 2 \times 10^5 \) for polystyrene (246) and \( 3.6 \times 10^5 \) for poly(\( \alpha \)-methylstyrene) (247) indicate that molecular weights below 10,000 will considerably affect \( T_g \). For this reason the DSC \( T_g \) determinations were carried out on samples with molecular weights of 15,000 or above.

Determination of the glass transitions of the graft copolymers by DSC (Du Pont 900) was only partially successful. In many cases only the soft phase \( T_g \) could be measured, this is because the technique will only detect discrete transitions and as will be shown in section 4.14 the hard phases very often have broad transitions.
4.13 DYNAMIC MECHANICAL STUDIES - General Considerations

It was mentioned in section 2.7 that on thermodynamic grounds the mixing of different high molecular weight polymers does not usually occur. The dynamic mechanical trace obtained for an SBR/polystyrene blend (sample Bl), figure 4.43, shows two distinct damping peak maxima (tan $\delta_{\text{max}}$) consistent with a two phase system. The temperature at which tan $\delta_{\text{max}}$ occurs is often referred to as the mechanical $T_g$ ($T_g'$) and is usually 5 to 15°C higher than the conventional $T_g$ when measurements are taken at a frequency of 0.1 to 1.0 Hz (156). Comparing the $T_g'$ values obtained in figure 4.43 with the $T_g$ values for SBR and polystyrene given in table 4.21, the damping peak values are higher by 18 and 27°C, respectively.

The broadness of the peaks and the large amount of damping between them suggests that a certain degree of compatibility exists between the phases. Measurement of half-peak widths can be used as a semi-empirical evaluation of the extent of mixing. The heights of the peaks can be used as an estimate of the relative amounts of each phase present, however, the values can only be taken as a rough guide because morphology also has a strong influence on the relative peak sizes.

The storage modulus ($E'$) versus temperature curve shows the expected sharp modulus changes in the vicinity of the mechanical glass transitions. The region between the damping peaks shows a gradual decrease in modulus with temperature.

The extent of rubber reinforcement by the inclusion of the hard phase can be determined from the relaxation strength which is proportional to the area under the tan $\delta$ curve and can be represented by $(E_U - E_R)/2(E_U/E_R)^{1/2}$ where $E_U$ and $E_R$ are the unrelaxed and relaxed rubber moduli as shown in figure 2.5. The value obtained (0.10) is typical for a filler reinforced unvulcanised system at this particular hard phase loading (30% wt.).
Applying mechanical models (section 2.6.5) to fit the modulus data we can get some idea of the type of morphology present. For the SBR/polystyrene blend two models can fit the experimental results as shown in figure 4.44. Taking weight fractions as approximations of \( v_z \), model I represents an SBR matrix with the polystyrene (PS) as the dispersed phase \( (v_z = 0.3) \). In model II the rubber is the dispersed phase \( (v_z = 0.7) \). In this latter model the amount of parallel coupling is reaching the limits as a coupled system and therefore where values of \( \ell \) or \( \lambda \to 1 \) the results are rejected. Model I therefore gives a more realistic interpretation of the type of structure present, i.e. a rubber matrix with a dispersed (non discrete) polystyrene phase. The theoretical curve does not fit the experimental data exactly, this probably results from the choice of systems used to represent the pure phases. Taking a constant value of \( 3.8 \times 10^9 \) Pa for the modulus of the polystyrene phase over the temperature range covered, is a reasonable approximation. The choice of modulus values for the SBR phase were, however, obtained for a cross-linked SBR system with a similar styrene content and therefore the deviation which arises above room temperature can be likened to the difference between a linear and a crosslinked polymer as shown in figure 2.5.

Before discussing the DMTA results for the various graft copolymers, it is necessary to consider the phase separation possibilities. In each sample there can be up to three different polymer species present, i.e. ungrafted rubber (B), grafted rubber (BgA) and homopolymer (A). In addition to a completely mixed single phase system several phase separated structures may arise, four examples are given:

i) a two phase system in which all A and B species phase separate, including the individual components of BgA.

ii) a two phase system in which A and B phase separate and BgA mixes with the A phase.
Figure 4.44

Takayanagi model data superimposed on the log $E'$ DMTA trace for an SBR/polystyrene blend (sample Bl)

**Model I**
- **SBR Matrix**
- $\phi = 0.760$
- $\lambda = 0.390$

$v_2 = \phi \lambda = 0.30$

**Model II**
- **Polystyrene (PS) Matrix**
- $\phi = 0.701$
- $\lambda = 0.998$

$v_2 = \phi \lambda = 0.70$
iii) as above except BgA mixes with the B phase.
iv) a three phase system in which A, B and BgA each form a separate phase.

A typical DTA trace obtained for one of the 38H graft copolymer samples is shown schematically below.

The peak positions suggest a structure represented by (ii) above, it will, however, be shown later (section 4.14) that I is not solely due to ungrafted rubber. In several samples a third peak (III) was present and because of its close proximity to \( T_{g(A)} \) suggested a pure A phase.

The position of peak II will depend on the relative amounts of each component present - grafted and ungrafted material. The actual shape of the peak reflects the degree of mixing which in turn will depend on such factors as the amount of grafting, the molecular weights of the grafts (and homopolymer) and also sample history. It is probably the result of this latter parameter that peak III arises.

Phase mixing between homopolymer and graft copolymer arises because of a certain amount of compatibility between the two phases. From a thermodynamic point of view miscibility can be explained in terms of the solubility parameters of the polymers. In addition to the lattice theory expression for the enthalpy of mixing (\( \Delta_h \)) for a pair of homopolymers
(equation (2.98)) Scott (176) expressed $\Delta H$ for two non-polar homopolymers in the form

$$\Delta H = V(\delta_A - \delta_B)^2 V_A V_B$$

(4.36)

where $\delta_A$ and $\delta_B$ are the solubility parameters for homopolymers A and B.

Similar $\delta_A$ and $\delta_B$ values will produce small changes in $\Delta H$ and therefore will increase the likelihood of phase mixing as shown by equation (2.97). Polystyrene and poly($\alpha$-methylstyrene) have very similar $\delta$ values which account for their miscibility. Considering the SBR/polystyrene blend, figure 4.43, it can be seen that even for this phase separated system there are noticeable amounts of phase mixing. As mentioned in section 2.7 Heier (181) and Krause (178) predicted that the presence of chemical bonds between the phases promoted phase mixing. Heier (181) calculated the minimum molecular weights for polystyrene blocks in a styrene-butadiene-styrene block copolymer below which phase separation would not occur. These values were 2.5 to 5.0 times greater than the values required to produce phase separation in a mixture of the corresponding homopolymers because of the loss in configurational entropy due to the chemical bonding. Experimental results (172, 173) have confirmed Heier's prediction that phase separation only occurs in styrene-butadiene-styrene systems when the polystyrene blocks have a molecular weight of 6000 or above.

The introduction of polystyrene or poly($\alpha$-methylstyrene) grafts into the SBR structure will have two basic effects, firstly it will reduce the solubility parameter difference between the SBR and any homopolymer present and therefore increase the compatibility between the two components and secondly the presence of chemical bonds between the hard and soft phases will discourage phase separation.

Because the solubility parameters for polyisoprene (8.1) and poly-
styrene (9.1) are considerably different it is anticipated that phase mixing will be considerably less in polyisoprene-g-polystyrene systems.
4.14 DYNAMIC MECHANICAL STUDIES - Detailed Discussion

All measurements were carried out on moulded specimens, unless otherwise mentioned. The individual systems investigated were: SBR-g-poly-(α-methylstyrene), SBR-g-polystyrene, SBR-g-poly(α-methylstyrene-co-styrene) and polyisoprene-g-polystyrene.

4.14.1 SBR-g-poly(α-methylstyrene)

A concise summary of the results for the various samples measured is given in table 4.22, together with other relevant data obtained earlier. The results can be basically divided into two groups, those with three tan δ (max) peaks and those with two. Typical examples of three peak traces are given in figures 4.45 and 4.46. Considering sample G39 (figure 4.45) there are three well defined damping peaks at -38, 91 and 162°C, which suggest an SBR phase, a mixed phase and an α-methylstyrene phase, respectively. The results in table 4.22 indicate that three peak traces tend to occur when a low moulding temperature (< 165°C) has been used on a sample containing relatively high molecular weight polymer (> 18,000). At higher moulding temperatures or for samples with lower homopolymer molecular weights, only a two peak trace is obtained, as shown in figures 4.47 and 4.48. The position and width of this mixed phase peak will depend on the relative amounts of SBR and polymerised α-methylstyrene (graft or homopolymer) and to a lesser extent the molecular weight of this latter material. In general Tg increases as the α-methylstyrene content increases, especially when in the form of homopolymer, with the effect becoming more pronounced at higher molecular weight. This is the kind of behaviour expected for a composite Tg, i.e. adding more A to an A/B mixed phase will move Tg nearer to that of homopolymer A.

Although only a few of the mixed phase half-peak widths could be measured the results indicate that peak broadening increases as grafting
### TABLE 4.22

Dynamic Mechanical and Characterisation Data for SBR-g-poly(α-methylstyrene)

<table>
<thead>
<tr>
<th>Sample ref.</th>
<th>hard phase (%)(^a)</th>
<th>GE (%)</th>
<th>Graft mol. wt. (x 10^-3)(^b)</th>
<th>(\Delta)</th>
<th>moulding temp. (°C)</th>
<th>(T_g) (°C)(^d)</th>
<th>(\frac{1}{2}) Peak width (°C)(^d)</th>
<th>(\frac{E_u-E_h}{2(E_uE_h)^{\frac{1}{2}}}) x 10^2</th>
</tr>
</thead>
<tbody>
<tr>
<td>G31</td>
<td>24</td>
<td>66</td>
<td>25.0</td>
<td>1.0</td>
<td>145</td>
<td>-35</td>
<td>65 150</td>
<td>19</td>
</tr>
<tr>
<td>G33</td>
<td>35</td>
<td>77</td>
<td>46.0</td>
<td>1.0</td>
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<td>18.2</td>
<td>2.2</td>
<td>130</td>
<td>-37 ~100 158</td>
<td>17</td>
<td>-</td>
</tr>
<tr>
<td>G38</td>
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<td>70</td>
<td>43.0</td>
<td>1.2</td>
<td>210</td>
<td>-38</td>
<td>168</td>
<td>16</td>
</tr>
<tr>
<td>G39</td>
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<td>54</td>
<td>23.0</td>
<td>1.5</td>
<td>160</td>
<td>-38</td>
<td>91 162</td>
<td>17</td>
</tr>
<tr>
<td>G40</td>
<td>36</td>
<td>27</td>
<td>11.5</td>
<td>1.6</td>
<td>160</td>
<td>-33</td>
<td>126</td>
<td>-21</td>
</tr>
<tr>
<td>G42</td>
<td>34</td>
<td>67</td>
<td>11.2</td>
<td>3.6</td>
<td>210</td>
<td>-33</td>
<td>62</td>
<td>28</td>
</tr>
<tr>
<td>G43</td>
<td>27</td>
<td>62</td>
<td>11.5</td>
<td>2.3</td>
<td>190</td>
<td>-40</td>
<td>45</td>
<td>26</td>
</tr>
<tr>
<td>G46</td>
<td>27</td>
<td>64</td>
<td>19.1</td>
<td>1.5</td>
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<td>-33</td>
<td>61 144</td>
<td>16</td>
</tr>
<tr>
<td>G50</td>
<td>32</td>
<td>66</td>
<td>11.6</td>
<td>3.1</td>
<td>170</td>
<td>-41</td>
<td>80</td>
<td>32</td>
</tr>
<tr>
<td>G52</td>
<td>26</td>
<td>63</td>
<td>17.0</td>
<td>1.5</td>
<td>160</td>
<td>-41</td>
<td>72</td>
<td>26</td>
</tr>
</tbody>
</table>

\(a\) Hard phase (%) = \(\frac{\text{weight of styrene/α-methylstyrene polymerised (g)}}{\text{total weight of product}}\) x 100.

\(b\) Taken as homopolymer \(M_p(\text{obs})\).

\(c\) As defined in section 4.5.5.

\(d\) Peak assignments as mentioned in section 4.13.
Figure 4.42
DVA trace of SBR-g-Poly(α-methyl styrene) (sample 650)
efficiency and graft molecular weights decrease. However, in terms of compatibility between the separate phases of the graft copolymer, it was mentioned earlier that decreasing the molecular weight and increasing the number of chemical linkages between the phases favours miscibility and therefore a sharpening of the tan δ peak. Because sample history is an important contributor to broadening some of the unexpected broadening effects may arise as the result of this.

Sample history is not restricted to the moulding temperature and pressure, but includes the solvent systems used in the actual synthesis and the recovery procedure. The rate at which the samples are precipitated from solution may also have an effect, therefore to infer that damping peak broadening is solely related to chemical structure would be a gross oversimplification. This is highlighted by comparing the DMA traces for a moulded sample of G38 (figure 4.48) with that for a solvent (chloroform) cast sample of G38 (figure 4.49). Although the peaks are in approximately the same positions, there is a considerable reduction in the size of rubber phase damping peak and in increase in the high temperature peak in the latter sample, which suggests that there is greater mixing between the phases. There is also a small peak at approximately 55°C in the solvent cast trace which is not present in the moulded sample trace. The position of this peak suggests a second mixed phase but with a different composition to that of the main peak.

The low temperature damping peaks listed in table 4.22 are found at -36 ± 4°C. Measurement of a pure SBR sample gave a Tg at -37°C and for SBR in a blend (sample B1, figure 4.43) a Tg at -34°C. The relative stability of this damping peak position indicates that it is primarily a pure rubber phase. The increases in half-peak widths for samples with low graft molecular weights (<12000) suggests that a small amount of mixing does occur.
TEMP. (°C)
In figure 2.1 we see that for an average of one graft per chain 37% of the total number of polymer chains will have no grafts. Similarly, for an average of two grafts per chain 15% of the polymer chains will be ungrafted. Because the average number of grafts per chain ($A'$) is low for the samples given in table 4.22 (10-36) it could be said that the rubber phase is composed of ungrafted SBR only, with the SBR-poly(α-methylstyrene) forming a mixed phase with the homopolymer. The positions of the mixed phases, however, suggest that some of the SBR in the graft copolymer must be present in the pure rubber phase.

Some insight into the extent of rubber reinforcement by the presence of poly(α-methylstyrene) can be gained from the relaxation strength results. Increasing the hard phase content will increase the load bearing capacity of the system which will ultimately result in a reduction in the relaxation strength of the rubber phase. Although the results do generally show this, the contributions from two other sources do not make it immediately obvious. For comparable hard phase loadings reinforcement is poorer with the lower molecular weight poly(α-methylstyrene) species, large relaxation strengths being obtained when grafting efficiencies are low. This would account for the large difference between an SBR/poly(methylstyrene) blend and a graft copolymer sample of similar hard phase content.

Application of the Takayanagi model (168) to the present system is illustrated by two samples having vastly different molecular weights and grafting efficiencies (G38 and G40), as shown in figure 4.50. Although neither of the theoretical curves is an identical fit, the correlations are sufficient to give an indication of the type of morphology present. Sample G38 shows a very small modulus decrease with temperature suggesting a heavily reinforced structure. The best theoretical fit is for a hard phase matrix with rubber inclusions. However, this is based on a model where SBR and poly(α-methylstyrene) are in separate phases with the
Takayanagi model data superimposed on the log $E'$ data traces for SBR-g-poly($\alpha$-methylstyrene)
(a) Poly($\alpha$-methylstyrene) (PMS) matrix with SBR as the dispersed phase (sample G38)
(b) SBR matrix with PMS as the dispersed phase (sample G40)
volume fraction values taken for the pure phases and as we have already found with these particular systems complete phase separation of the two components does not occur. Therefore, to construct a true model it would be necessary to not only determine the amount of mixed phase present but also obtain modulus/temperature data for the mixed system. Nevertheless, the pure phase equivalent model does suggest that for this particular sample the mixed phase is the continuous phase and that the pure rubber phase is dispersed within it. Sample G40 shows a much larger modulus drop over the same temperature range and as a result can be represented by a model whereby the rubber is the continuous phase. The large amount of parallel coupling does, however, suggest that the mixed phase is semi-continuous. These models imply that a lamellar type morphology predominates (see section 2.7).

Attempts to relate the increased modulus values for the rubber phase, at temperatures between the T_g values, with filler type effects using equations (2.91) and (2.92) gave modulus values considerably lower than obtained by DMTA. This suggests that the hard phase contribution to modulus is greater than can be accounted for by interpreting as a filler reinforced system only.

4.14.2 SBR-g-polystyrene

DMTA results for four samples are summarised in table 4.23. In each case only two loss peaks were present, a typical trace of a moulded sample is given in figure 4.51. Although suggesting a two phase system, the position of the high temperature damping peak, even allowing for molecular weight effects (equation (2.90)), does not correspond to a pure styrene phase. Therefore some degree of mixing between the styrene and SBR phases must occur and because grafting efficiencies are high for these samples, this mixing is between the constituents of SBR-g-polystyrene only. Using
### TABLE 4.23

Dynamic Mechanical and Characterisation Data for Several Graft Copolymers

<table>
<thead>
<tr>
<th>Sample ref.</th>
<th>hard phase (%)(^a)</th>
<th>GB (%)</th>
<th>Graft mol wt. (x 10(^{-3}))(^b)</th>
<th>A(^c)</th>
<th>moulding temp. (°C) or casting solvent</th>
<th>(T_\beta) (°C)(^d)</th>
<th>(\Delta h) Peak widths (°C)(^d)</th>
<th>(E_u/E_r) x 10(^2)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>I</td>
<td>II</td>
<td>III</td>
</tr>
<tr>
<td><strong>SBR-g-polystyrene</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>G10</td>
<td>31</td>
<td>~100</td>
<td>6.2(^e)</td>
<td>8.6(^e)</td>
<td>chloroform</td>
<td>-32</td>
<td>65</td>
<td>-</td>
</tr>
<tr>
<td>G19</td>
<td>38</td>
<td>95</td>
<td>7.6</td>
<td>8.7</td>
<td>110</td>
<td>-36</td>
<td>67</td>
<td>-</td>
</tr>
<tr>
<td>G20</td>
<td>33</td>
<td>89</td>
<td>10.0</td>
<td>5.2</td>
<td>105</td>
<td>-33</td>
<td>70</td>
<td>-</td>
</tr>
<tr>
<td>G21</td>
<td>38</td>
<td>94</td>
<td>4.8</td>
<td>14.1</td>
<td>100</td>
<td>-32</td>
<td>36</td>
<td>-</td>
</tr>
<tr>
<td><strong>SBR-g-poly((\alpha)-methylstyrene-co-styrene)</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>G70</td>
<td>50</td>
<td>71</td>
<td>9.2</td>
<td>9.0</td>
<td>chloroform</td>
<td>-40</td>
<td>49</td>
<td>-</td>
</tr>
<tr>
<td>G85</td>
<td>23</td>
<td>82</td>
<td>4.5</td>
<td>6.2</td>
<td>chloroform</td>
<td>~24</td>
<td>~60</td>
<td>-</td>
</tr>
<tr>
<td><strong>Polyisoprene-g-polystyrene</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>GB</td>
<td>31</td>
<td>?</td>
<td>6.4(^f)</td>
<td>9.9(^f)</td>
<td>110</td>
<td>-48</td>
<td>80</td>
<td>-</td>
</tr>
</tbody>
</table>

\(\text{a-d)}\) As in table 4.22.

\(\text{e)}\) See table 4.11.

\(\text{f)}\) See table 4.3.
equation (2.89) we can obtain an approximate value for the weight fraction of SBR necessary, in the mixed phase, to lower the mechanical $T_g$ of polystyrene to the value given, the pure phase mechanical $T_g$ values were taken from figure 4.44. The weight fraction obtained was 0.26, which, compared to the total SBR weight fraction in the polymer of 0.63, implies that most of the SBR is present in the rubber phase (low temperature damping peak). The actual position of $T_g$ for this phase indicates a pure SBR phase. It is unlikely, however, in view of the large average numbers of grafts per chain (5.2-9.3) and the large amount of material contributing, that this phase is due only to ungrafted material and therefore some phase separation of the individual components of SBR-\text{g}-polystyrene must occur.

The DMTA trace for a sample cast from chloroform, G10 (figure 4.52), shows much greater mixing between the phases (larger tan $\delta$ values) than that found with the moulded samples of similar styrene content, e.g. sample G19 (figure 4.51), which suggests that solvent casting tends to promote phase mixing.

Comparing the relative positions of the mixed phase damping peaks in each of the samples measured, we find that a decrease in the polystyrene content or molecular weight produces, as expected, a corresponding drop in $T_g'$. Due to a certain amount of peak overlap, as a result of the close proximity of the two peaks, only comparisons of the large (mixed phase) damping peaks can be made. It would appear from the half-peak widths that broadening increases with an increase in graft molecular weight, i.e. there is greater compatibility between SBR and polystyrene in the graft copolymer when the latter has a low molecular weight, this can be likened to the styrene-butadiene-styrene system (see section 2.7) where at a particular low polystyrene molecular weight phase separation will not occur.

The relaxation strength results show similar trends to the SBR-\text{g}-
poly(α-methylstyrene) systems where reinforcement increases as the amount and molecular weight of the grafted polymer increases.

Applying the Takayanagi model to the SBR-g-poly styrene systems produces very similar results to those found for the α-methylstyrene graft copolymers, e.g. for sample G21 the best theoretical fit was for a rubber matrix with \( \phi = 0.95 \) and \( \lambda = 0.41 \) \((v_2 = \phi\lambda = 0.38)\). Therefore the mixed hard phase shows considerable reinforcement of the rubber matrix.

4.14.3 SBR-g-poly(α-methylstyrene-co-styrene)

A summary of the results for the two solvent cast samples measured is given in table 4.23. The DMA trace for sample G70 is given in figure 4.53. A striking feature of the tan δ traces for these samples is the very small low temperature damping peaks, as found for other solvent cast samples (figures 4.49 and 4.52) and therefore confirms that solvent casting favours greater miscibility between the phases and therefore reduces the amount of rubber phase.

Because the hard phase damping peaks are due to a mixture of SBR and styrene/α-methylstyrene copolymer, it was not possible to investigate the effect of the grafting copolymer composition on hard phase \( T_g \). It was, however, evident that the presence of SBR in the hard phase can considerably reduce the \( T_g \) as indicated by the low values obtained, compared to those of the pure hard phases.

The differences in relaxation strengths for the two samples can be related to the amount of mixed phase material contributing to the reinforcement of the rubber phase which in turn will depend on the amount of 'pure' hard phase material used, i.e. the larger relaxation strength is obtained for the sample with the lowest styrene/α-methylstyrene content (G65).
Applying the Takayanagi model to the more rubber sample (G65), the best theoretical fit of the modulus data is for a rubber matrix with $\phi = 0.90$, and $\lambda = 0.25$ ($v_2 = \phi \lambda = 0.23$). It is clear that even when the original hard phase content is relatively low the amount of mixed hard phase is sufficient to take nearly all of the applied stress.

4.14.4 Polyisoprene-g-polystyrene

Only one of the samples prepared was suitable for mechanical testing, sample G8. The DMTA trace for a moulded specimen is given in figure 4.54 and the summarised results given in table 4.23. The sharp tan $\delta$ peak obtained at low temperature suggests a pure polyisoprene phase with the second rather broader peak at 80°C corresponding to a polystyrene phase. In view of the broadness and actual location of this peak, and allowing for low molecular weight effects, it is unlikely that a pure polystyrene phase is present, therefore, a small amount of polyisoprene must be present in this phase. The mixing is, however, considerably less than that observed in the other systems.

Although no grafting efficiency values were obtained for the polyisoprene graft copolymers the g.p.c. trace for sample G8 did suggest a high grafting efficiency, this together with the calculated average number of graft sites per chain implies that the rubber phase is primarily due to phase separated polyisoprene-g-polystyrene and not ungrafted material.

For the amount of hard phase material present the fairly large relaxation strength suggests that the hard phase does not contribute to the reinforcement of the rubber as though a continuous phase, as suggested by the relaxation strength values for some of the samples given in tables 4.22 and 4.23.
Figure 4.4
DTA trace of polystyrene-g-polysoprene (sample G5)
Tensile stress ($\sigma_b$) and elongation at break ($\varepsilon_b$) data for the samples measured are given in table 4.24. The types of stress-strain behaviour observed can be represented by the three examples given in figure 4.55. The trace for an SBR/polystyrene blend is illustrated by sample B1 which has poor $\sigma_b$ and $\varepsilon_b$ values. In the absence of polystyrene the unvulcanised SBR is too weak to measure and therefore the addition of polystyrene does improve its tensile properties, however, only to the extent of acting as a high modulus filler, producing a poor strength 'plastic like' material. The graft copolymer samples however exhibit distinctive elastomeric properties. Sample G36 has an initial high modulus (large $\sigma$, small $\varepsilon$) which is followed by a yield point, a small amount of draw and then an elastic extension. This is typical of several of the moulded samples measured (G20, G33, G50 and G58). Sample G42 shows an initial high modulus but there is no well defined yield point or excessive drawing. This trace is typical of the solvent cast samples (G10 and G65) and some of the moulded samples (G8, G10 and G43).

These results can be best explained if we first consider the stress-strain behaviour of a styrene-butadiene-styrene block copolymer system in which the styrene content is varied (172) as shown in figure 2.13. The gradation of properties with styrene content is apparent. At a very low styrene content (13% wt.) the block copolymer behaves as an undercured rubber. On increasing the content to 28% wt. the block copolymer exhibits the stress-strain characteristics similar to a vulcanised rubber. At higher styrene content (39 and 53% wt.) yield points become apparent and there is considerable drawing before elastic behaviour ensues. At even higher styrene content (65% wt.) a very high yield stress is followed by a short draw and immediate break. The highest styrene content sample
### TABLE 4.24

Physical Property Data Obtained for Several Graft Copolymers

<table>
<thead>
<tr>
<th>Sample ref. a</th>
<th>Tensile strength ( \sigma_b ) (MPa)</th>
<th>Elongation at break ( \varepsilon_b ) (%)</th>
<th>Compression set (%)</th>
<th>Hardness (Shore A)</th>
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</thead>
<tbody>
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<td>G8</td>
<td>8.6</td>
<td>1600</td>
<td>72</td>
<td>78</td>
</tr>
<tr>
<td>G10 b</td>
<td>5.9</td>
<td>790</td>
<td>69</td>
<td>85</td>
</tr>
<tr>
<td>G19</td>
<td>8.1</td>
<td>300</td>
<td>69 (24)</td>
<td>92</td>
</tr>
<tr>
<td>G20</td>
<td>5.9</td>
<td>370</td>
<td>43 (5)</td>
<td>89</td>
</tr>
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<td>G31</td>
<td>-</td>
<td>-</td>
<td>54 (9)</td>
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<td>10.7</td>
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<td>93</td>
</tr>
<tr>
<td>G34</td>
<td>-</td>
<td>-</td>
<td>74</td>
<td>94</td>
</tr>
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<td>-</td>
<td>78</td>
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<td>90</td>
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<td>G40</td>
<td>-</td>
<td>-</td>
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<td>-</td>
<td>71</td>
</tr>
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<td>G46</td>
<td>-</td>
<td>-</td>
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<td>88</td>
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<td>G50</td>
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<td>660</td>
<td>-</td>
<td>85</td>
</tr>
<tr>
<td>G52</td>
<td>-</td>
<td>-</td>
<td>51 (4)</td>
<td>85</td>
</tr>
<tr>
<td>G65 b</td>
<td>6.0</td>
<td>880</td>
<td>-</td>
<td>66</td>
</tr>
</tbody>
</table>

Values in ( ) are the compression set values taken after a recovery period of 6 days.

a) Polyisoprene-\( \alpha \)-polystyrene

- SBR-\( \alpha \)-polystyrene
- SBR-\( \alpha \)-poly(\( \alpha \)-methylstyrene)
- SBR-\( \alpha \)-poly(\( \alpha \)-methylstyrene-co-styrene)

b) Samples cast from chloroform.
Typical examples of the stress-strain curves obtained

FIGURE 4.55
Stress-strain curves for a sample (G65) measured under cycling loading

FIGURE 4.56
(80% wt.) behaves very much like pure polystyrene. In general the yield stress and tensile strength rise as the concentration of styrene units increases. Similar behaviour has been found with styrene-isoprene-styrene block copolymer systems.

The differences in tensile behaviour can be related to the polymer morphology and as mentioned in section 2.7 the morphology of an ABA block copolymer is primarily determined by its composition. It was also mentioned that sample history also plays a role, however, for the present discussion let us only consider a styrene-butadiene-styrene block copolymer slowly cast from a good solvent for both block types. Below about 30% wt. styrene content spherical morphology persists (see section 2.7). This is similar to Meier's predicted molecular weight ratio range for spherical morphology in an AB block copolymer (figure 2.15). It is this morphological form which is primarily responsible for the high tensile strengths and elongations at break that are often obtained with these copolymers as shown by the stress-strain curve for the 28% wt. styrene sample in figure 2.13. At very low styrene contents the styrene block molecular weight becomes too small for effective phase separation to occur, as predicted by Meier, and therefore poor strength materials are obtained, as shown by the 12% wt. styrene content sample. Beyond a 30% wt. styrene content the domains become too large to exist as discrete spherical domains and a continuous or semicontinuous morphological form, predominates, i.e. rods or lamellae. The materials then begin to exhibit 'plastic like' behaviour as shown by the yield points and drawing observed with the high styrene content samples. The yield point can be regarded as a particular value of stress and strain beyond which an irreversible deformation occurs. The actual shape of these stress-strain curves becomes a function of the reinforcement effect of the styrene, which is itself governed by the 'degree of ordering' in the system. It is therefore apparent that for samples with a styrene content of 30% wt. and above,
where morphology can vary considerably, sample history then becomes an important factor.

The yield point characteristics observed with several of the graft copolymer samples prepared in the present work suggests that the hard phase to some extent exists as a continuous phase, as mentioned in section 4.14. Although the samples generally have a high hard phase content (> 30% wt.) the true hard phase of the material could be higher than this due to phase mixing.

Because yielding can be regarded as the breakdown of the continuous glassy phase the absence of yield points for several samples tested suggests that the hard phase can exist as a discrete phase and which is not necessarily restricted to samples with low hard phase contents, e.g. G8, G10, G19 and G42.

Cyclic testing was carried out with sample G65, two stress-strain curves obtained during loading, with only a short rest period between, are given in figure 4.56. The drop in stress at comparable elongations in the second cycle is due to stress softening - 'Nullins effect' - and is a characteristic feature of filled rubbers (249) and ABA thermoplastic elastomers (250). In the latter systems this stress softening has been attributed to the slippage of load bearing chains. It was found by Beecher et al. (190) that in the absence of a yield point the initial stress-strain properties returned when the samples were allowed to relax at the test temperature for long periods of time. This reversibility in mechanical properties suggests that stress softening is not caused by chain scission which would degrade the copolymer molecule. It was also observed by the above workers (190) that samples which exhibited yield points in their initial stress-strain curves showed considerable stress softening in a second cycle and the absence of a yield point. The original stress-strain properties for these samples did not return when
allowed to relax. The stress softening in this case was attributed not only to chain slippage but also to an irreversible breakdown of the continuous/semicontinuous phase structure (mentioned earlier) and plastic deformation of the domains (190, 251). From the stress-strain curves shown in figure 4.55, and the behaviour of sample G65 under cyclic loading, figure 4.56, it is apparent that the above interpretation can equally apply to the present systems.

To compare the ultimate properties of the various polymer systems with each other and with other elastomer systems, the results given in table 4.24 are superimposed on the failure envelopes for vulcanised SBR (252) and a commercial styrene-butadiene-styrene block copolymer (251), as shown in figure 4.57. Some of the data given in table 2.2 are also plotted.

The tensile strengths ($\sigma_b$) of the graft copolymer tested lie within a fairly narrow band of values, with the lower ones, irrespective of 'pure' hard phase content, generally being associated with styrene grafted samples. This tends to suggest that the presence of homopolymer improves $\sigma_b$ (little or no homopolymer was present in the sample where styrene was the grafting monomer).

The elongation at break ($\epsilon_b$) values covered a wide range, with the moulded SBR-g-polystyrene having the poorest values. The SBR-g-poly($\alpha$-methylstyrene) results were all fairly closely grouped together at slightly higher $\epsilon_b$ values. A further increase in $\epsilon_b$ was noticeable with the solvent cast samples (G10 and G65). The only polyisoprene-g-polystyrene sample (G8) tested had an $\epsilon_b$ value considerably higher than any of the other samples.

These results, in general, suggest that the more ordered the phase structure or the greater the incompatibility of the phases the better the ultimate properties. No correlation could, however, be obtained between
The tensile strength ($\sigma_t$) and elongation at break ($\varepsilon_b$) for data given in table 4.24 are superimposed on the failure envelopes for unfilled vulcanised SBR and a styrene-butadiene-styrene block copolymer.
the average number of grafts per chain or the graft molecular weight and the ultimate properties.

From figure 4.57 it can be seen that most of the moulded SBR-g-poly-(\(\alpha\)-methylstyrene) samples have properties comparable to vulcanised SBR. Adding reinforcing fillers to SBR vulcanisates shifts the failure envelope along the tensile strength axis only (252) and therefore these SBR graft copolymers can also be regarded as filler reinforced SBR systems. The styrene-butadiene-styrene block copolymer failure envelope located at higher elongations for comparable \(\sigma_D\) values shows their better tensile properties compared to the present SBR systems, which possess a greater degree of phase mixing and hence a more disordered structure. This argument also applies to the star and graft copolymers of styrene and butadiene also given in figure 4.57. Only the solvent cast SBR samples (G10 and G65) have ultimate properties comparable with those of the styrene/butadiene block copolymer systems, which suggests that solvent casting produces a more ordered phase structure than that obtained for moulded samples.

To achieve superior ultimate properties over the styrene-butadiene-styrene systems as found with polyisoprene-g-polystyrene sample (G8) implies that not only must the sample possess spherical morphology but there must also be greater bonding between the phases; a possible consequence of a grafted system. The difference in properties between this sample and the SBR graft copolymers may reflect the greater incompatibility of the phases in polyisoprene-g-polystyrene.
4.16 COMPRESSION SET

For elastomeric materials used in load bearing applications, compression set values of up to 20% at 20°C are considered acceptable (BS2494 (1976)). The results given in table 4.24 are, however, considerably higher than this, with some values reaching between 70 and 80%. This form of stress relaxation is due to the deformation of the hard phase which acts as the crosslinking for the rubber phase. The recovery time of thirty minutes, considered sufficient to accurately measure the amount of set in a vulcanisate, is not, however, sufficient for thermoplastic elastomers where much longer recovery times are required. Measurements of the percentage recovery showed a fairly linear increase with time over a period of several hours.

After several days' recovery the compression set values were considerably reduced as shown by the values given in brackets, table 4.24. The high compression set values at short times are due to the high deformation of the mixed phase material which has T_g relaxation in the region of room temperature and therefore the recovery times of this deformation will be long.

In view of the range of compression values used as a result of the variation in the original sample thickness and also the differences in time scales between dynamic mechanical and compression set measurements, no correlations between tanδ or modulus and compression set, could be established.
4.17 HARDNESS

The Shore A values given in table 4.24, for the range of 'pure' hard phases present (23-38% wt.) are higher than expected when compared with the corresponding styrene-butadiene-styrene rubbers (4). This further emphasises that the hard phase contributes to the structure partly as a continuous phase, which arises primarily because of the presence of a mixed as opposed to pure hard phase.

Because hardness measuring can be regarded as a short term creep experiment where creep compliance is given by equation (2.75), the time dependent modulus value will be approximately proportional to \((100-H)^{-1}\) for very small measurement times, where \(H\) is the hardness value (Shore A scale: 0-100). Taking the modulus values at 20°C from the DMTA results a plot of log modulus against log \((100-H)\) is given in figure 4.58. It can be seen from these results that there is good correlation between the DMTA determined modulus values and the Shore A hardness values.
FIGURE 4.58
Plot of log $E'$ values at $20^\circ$C, obtained from DMA results, against log $(100-R)$, where $R$ is the hardness value given in Shore A units.
CHAPTER 5

CONCLUSION

The preparation of polyisoprene, polyisoprene-\(\alpha\)-polystyrene and polyisoprene-\(\alpha\)-poly(\(\alpha\)-methylstyrene) indicated that anionic polymerisation and grafting procedures could be successfully carried out using a combination of high vacuum and argon blanket techniques. Following these procedures it was possible to graft a commercial un Vulcanised rubber, SBR (Soprene 1204) with polystyrene, poly(\(\alpha\)-methylstyrene), poly(\(\alpha\)-methylstyrene-co-styrene) and poly(vinyltoluene).

SBR-\(\alpha\)-polystyrene copolymers prepared in hydrocarbon solvent were obtained in yields in excess of 80% for polymerisations carried out for 8 hours or more at room temperature. Grafting efficiencies, determined from the amount of homopolymer present in the product g.p.c. traces, were also high (> 80%) for these systems when metalation with the \(\alpha\)-BuLi:TMEDA complex was carried out for at least 12 hours. Shorter metalation and polymerisation periods resulted in lower grafting efficiencies and poorer yields.

The low temperature requirement for the polymerisation of \(\alpha\)-methylstyrene prevented SBR-\(\alpha\)-poly(\(\alpha\)-methylstyrene) from being prepared in a hydrocarbon only solvent system because both grafting and homopolymer studies of \(\alpha\)-methylstyrene in methylcyclohexane and methylcyclohexane/cyclohexane have shown that little or no polymer is produced at low temperature (\(\lesssim\) 40°C) in these solvents even after polymerisation periods of up to 72 hours. When THF was used as solvent or cosolvent \(\alpha\)-methylstyrene did polymerise at low temperature, however, it was found that prolonged exposure of initiator and 'living' polymer species to THF, at room temperature, produced inactive materials and therefore all metalation reactions had to be performed in the absence of this solvent. The prepara-
tion of SBR-g-poly(α-methylstyrene) was achieved by first carrying out the metalation reaction in a hydrocarbon solvent only and then adding THF prior to low temperature polymerisation. To obtain yields of 80% or above, within 24 hours, it was necessary to perform the reactions at -70°C in the presence of at least 30 vol. THF. To obtain similar yields at higher temperatures or with smaller amounts of THF present, considerably longer polymerisation times were required. Rate studies of α-methylstyrene polymerisation suggested that poorer yields at higher temperatures were due to kinetic rather than monomer equilibrium effects. Grafting efficiencies for SBR-g-poly(α-methylstyrene) were generally found in the 60 to 80% range.

Degradation of the SBR backbone in the graft copolymer by ozonolysis techniques and the subsequent analysis of the products by g.p.c. indicated that grafting polymer and homopolymer, produced as the result of inefficient grafting, had similar molecular weights and therefore for all samples where homopolymer was present the molecular weight of this species could be taken to represent that of the grafts. The molecular weights of polystyrene, present in SBR-g-polystyrene preparations, were in reasonable agreement with the calculated graft molecular weights based on the amount of 'active' initiator added, however, larger than anticipated molecular weight values for homopolymer, present in SBR-g-poly(α-methylstyrene) preparations, suggested that a proportion of the initiator was rendered inactive. A reaction with THF or impurities present in this solvent was not considered to be wholly responsible for these discrepancies because the grafting of SBR with a styrene/α-methylstyrene mixture in the presence of THF produced results similar to those obtained for SBR-g-polystyrene. The apparent reduction in grafting efficiency and 'active' initiator for the α-methylstyrene only SBR grafting systems, may be attributable to steric hindrance effects which severely restrict the number of graft sites available to the monomer.
Grafting SBR with vinyltoluene gave results comparable with those for the SBR-g-polystyrene system.

With regard to the mechanical properties, DMTA studies of the SBR graft copolymers have shown that complete phase separation between backbone rubber and grafting polymer does not occur. Separate hard and soft phases do exist, however, the position and shape of the hard phase tanδ damping peak suggests a mixed phase comprising of graft/homopolymer and a small amount of SBR. The presence of the rubber increases the relative amount of hard phase and lowers the hard phase Tg, producing materials with higher hardness (Shore A) values and lower softening temperatures than expected if phase separation had been complete.

The tensile strength and elongation at break values obtained for the SBR graft copolymers, although comparable with those for a conventional SBR vulcanisate, were slightly lower than those for a styrene-butadiene-styrene system probably as a result of poorer phase separation. For a system where phase separation appeared to be almost complete, polyisoprene-g-polystyrene, very good ultimate properties were obtained, especially, elongation at break.

Compression set results for the SBR graft copolymers were generally, poor, however, because of the slow recovery processes involved, a feature usually associated with styrene-butadiene-styrene systems, the measurements obtained were not a true reflection of the amount of set.

The major advantage of thermoplastic elastomers of the SBR graft copolymer type over styrene-butadiene-styrene block copolymers and related systems is the simplified synthesis procedure. The use of a preformed polymer backbone not only reduces the number of stages in the process but also reduces the likelihood of premature termination effects.
REFERENCES


46. R.C.P. Cubbon and D. Margerison, Polymer, 6, 102 (1965).


85. Solprene 406, 414, 416 and 418 (Phillips Petroleum Co.).


113. Sun Oil Co., British Pat., 1,121,195 (July 1968).


115. A.F. Halasa and D.P. Tate, British Pat., 1,210,088 (October 1970).


203. J. Young and Co., Acton, U.K.


210. G. Yeaton (Loughborough University), private communication.


230. F. McInnes, (Philips Petroleum Co. (UK) Ltd.), private communication.
Copolymer Nomenclature

For a block copolymer composed of monomers A and B only, several structural types are possible.

<table>
<thead>
<tr>
<th>COPOLYMER TYPE</th>
<th>STRUCTURE</th>
<th>SYMBOL</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diblock</td>
<td>AAAAABBBB</td>
<td>AB</td>
</tr>
<tr>
<td>Triblock</td>
<td>AAAABBBB</td>
<td>ABA</td>
</tr>
<tr>
<td>Multiblock</td>
<td>AAAABBBB</td>
<td>(AB)_n</td>
</tr>
<tr>
<td>Star block</td>
<td>AAAABBBB</td>
<td>(AB)_nX</td>
</tr>
<tr>
<td>Graft</td>
<td>....BBBBB</td>
<td>BgA</td>
</tr>
</tbody>
</table>

Copolymers are named using IUPAC notation. Several examples are given below.

<table>
<thead>
<tr>
<th>COPOLYMER TYPE</th>
<th>EXAMPLE (IUPAC nomenclature)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AB</td>
<td>polystyrene-b-polybutadiene</td>
</tr>
<tr>
<td>ABA</td>
<td>polystyrene-b-polybutadiene-b-polystyrene (styrene-butadiene-styrene)</td>
</tr>
<tr>
<td>BgA</td>
<td>polyisoprene-g-poly(α-methylstyrene)</td>
</tr>
<tr>
<td>BgA</td>
<td>poly(styrene-s\textsuperscript{a}-butadiene)-g-polystyrene (SBR-g-polystyrene)</td>
</tr>
</tbody>
</table>

Abbreviated names, where used, are given in ( ).

a) \( -s \) represents a statistically random copolymer. Where the extent of block formation or randomness is uncertain \(-co\) is used.