Comb graft copolymers: synthesis, micellisation and dispersant behaviour

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COMB GRAFT COPOLYMERS: SYNTHESIS,
MICELLISATION AND DISPERSANT BEHAVIOUR

by

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A Doctoral Thesis
submitted in partial fulfilment of the requirements
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To my wife Marie
and my Parents

"First the test tube, then the pail
Then the semi-working scale
Even bigger, ever faster,
faster, faster, then - disaster!"

Parkes.
ABSTRACT

Styryl-terminated polystyrene macromonomers have been synthesised by the anionic polymerisation of styrene. Initiation was by sec-butyl lithium; termination involved the addition of diphenylethylene prior to vinyl benzyl chloride. Characterisation of the macromonomers was performed using gel permeation chromatography (GPC) and proton nuclear magnetic resonance spectroscopy (nmr).

Novel comb graft copolymers were synthesised by the copolymerisation of the macromonomer with a comonomer. The following comonomers were used: 2-vinylpyridine (2-VP), 4-vinylpyridine (4-VP) and N-(vinylbenzyl)pyrrolidone (VBP). Graft copolymers were made with a range of compositions by varying the feed ratios of the comonomer to the macromonomer. Reactivity ratios were determined for the different graft copolymer systems and compared to the simple statistical copolymerisation of styrene with comonomer. Characterisation of the graft copolymers was performed using GPC, nmr and membrane osmometry.

Micellar dispersions of the comb graft copolymers were prepared in cyclohexane, toluene and methanol. These were subsequently characterised by small-angle X-ray scattering (SAXS) and transmission electron microscopy (TEM). Micellar behaviour was related to graft copolymer composition and structure.

The graft copolymers were subsequently used as steric stabilisers in dispersion polymerisations of bis-hydroxyethyl terephthalate in high boiling aliphatic hydrocarbon, methyl methacrylate in cyclohexane, vinyl pyridine in toluene/cyclohexane and styrene in methanol. A number of parameters have been investigated including initiator, stabiliser and monomer concentrations. Graft copolymer composition and structure were shown to be important factors
for the effective steric stabilisation of polymer particles in conjunction with information on surface coverage data.
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1. INTRODUCTION

A number of methods are available for preparing polymer particles within an inert medium. The most widely studied and commercially exploited system is emulsion polymerisation. Emulsion polymerisation can be used to prepare high molar mass addition polymers at high concentration whilst retaining a relatively low viscosity in the reactor. These properties have allowed extensive use of addition polymers in a variety of industries, notably in surface coatings. Water as an inert reaction medium is cheap, non-toxic and non-flammable, but has disadvantages when used in surface coatings such as slow and uncontrollable rates of evaporation. Attention has therefore, focused over the last twenty five years on the use of non-aqueous dispersion polymerisation of addition polymers. Non-aqueous dispersion polymerisation is a useful technique not only in the surface coatings industry but also to the colloid scientist as it is possible to control the size and distribution of the polymer particles. These systems are therefore ideal for investigating aspects of colloid theory.

The stabilisation of particles in organic media is achieved by use of a barrier, generated by the interaction of "dissolved" polymer chains on the dispersed particles, i.e. by steric stabilisation. This attachment of polymeric dispersants to particles is achieved by several methods including acid-base interactions, covalent links and physical adsorption. Amphiphatic block copolymers are ideal for steric stabilisation of addition polymer particles, utilising physical adsorption processes by firm anchoring of the insoluble A block to the surface of the particle with the other soluble block extending into the liquid. Graft copolymers have also been used as effective stabilisers for polymer particles (see fig 1). The backbone generally, associates with the insoluble particle; this is known as the anchor block. The graft provides stabilisation by extending into the organic medium, thereby preventing flocculation. The anchor block must be insoluble in
FIGURE 1
THE STERIC STABILISATION OF MODEL POLYMER PARTICLES
USING PREFORMED COMB GRAFT COPOLYMERS

soluble stabilising grafts

particle

insoluble anchor block (A)
the continuous phase, so that it is adsorbed onto the particle surface. The effectiveness of the copolymer can be enhanced significantly by ensuring the anchor block is miscible with the dispersed particle. It has been shown that the composition of the anchor block does not have to be identical to the dispersed phase polymer. For example, Shakir\textsuperscript{6} and Taylor\textsuperscript{7} have extensively studied the dispersion polymerisation of methyl methacrylate using block copolymer stabilisers containing PS anchor components. It may be possible to rely only on the insolubility of the anchor component in the dispersion medium to drive it to the particle/medium interface. A number of other factors effect the dispersing action of the block or graft copolymers, including the copolymer composition, i.e. the relative lengths of the soluble and insoluble components; the actual lengths of the insoluble backbone and side chains; and finally the frequency of grafts or blocks.

Preformed block and graft copolymers can be prepared by a variety of methods\textsuperscript{8}. To fulfil the requirements for controlling graft copolymer structure in order to study their effectiveness as steric stabilisers in dispersion polymerisations, only a few methods are available. The synthesis of graft copolymers from the copolymerisation of macromonomers with conventional comonomers is one such method\textsuperscript{8,9,10}. Macromonomer molecules which copolymerise result in grafts, whereas the comonomer(s) which copolymerise essentially constitute the backbone of the resulting graft copolymers. By controlling the feed ratio in the copolymerisation it is possible to produce graft copolymers with well-defined and controlled compositions. The copolymerisation behaviour of macromonomers is disputed in the literature with conflicting reports of the ability of the macromonomer chain to affect the reactivity of its terminal polymerisable end-group\textsuperscript{9,11}. This has implications on the ability to control the chemical composition and chain architecture of the graft copolymers produced using this method.

- 2 -
Emulsion polymerisation is not suitable for the production of condensation polymers which require the removal of a by-product at elevated temperatures. Condensation polymers are prepared industrially using a melt polymerisation route. The monomers or precursors are heated until they melt and stirred. A vacuum is applied to aid the removal of the by-product such as a diol. As the polymerisation continues the viscosity of the molten polymer increases rapidly with increasing molar mass. Removal of by-product becomes increasingly difficult as the viscosity increases and a limiting molar mass is reached. The molar mass cannot be increased above this point because stirring of the reactor is difficult, and product quality deteriorates rapidly on continued heating. Attention has turned to the use of non-aqueous dispersion polymerisation to prepare high molar mass condensation polymers.4,12,13

The liquid reactants are dispersed in an aliphatic hydrocarbon and then polymerised in an emulsion or suspension form. The by-product of the step-reaction polymerisation is removed faster as the path length for the diffusion of the by-product is relatively short compared to conventional bulk processes. Therefore, the rate of polymerisation is faster compared to the bulk process. Other advantages are the lower overall viscosity of the system which is not dependant on molar mass of the final polymer and the higher molar masses produced by increasing reaction times without seriously affecting product quality.

In relation to the design of stabilisers for non-aqueous dispersion polymerisation of condensation polymers further requirements need to be met. The graft copolymer must not only provide stabilisation of the initial reactants when they are emulsified but also act as a dispersant for the particulate polymer produced, both throughout and after the polymerisation. The stabiliser must also not degrade at the elevated polymerisation temperatures (500-600K), and should not contain groups that will interfere with the polymerisation reactions.
Thus, the process puts severe demands on the design of possible dispersants.

Three different types of graft copolymer stabiliser were chosen, consisting of PS grafts and either poly(4-vinylpyridine), poly(2-vinylpyridine) or poly(N-(vinylbenzyl)pyrrolidone) backbones. Methods of synthesis of the PS macromonomer of a predictable molar mass and composition are known\textsuperscript{14}. The significantly different solubility parameters for the PS grafts to the backbone suggests they would be useful for stabilising polymer particles in hydrocarbon media. Low molar mass PS dissolves in heptane and hexane at elevated temperatures\textsuperscript{7}. It is envisaged that in any dispersion polymerisation process no problems with solubility of PS will be encountered. Thus, the PS grafts will provide an effective stabilising layer, and would be anchored to the particle by the insoluble backbone component.

A range of graft copolymers of differing composition but with a similar overall molar mass were synthesised using free radical copolymerisation. The molar mass of the grafts was kept constant at $M_n = 3.2 \text{ kg.mol}^{-1}$. Investigations were carried out into the behaviour of graft copolymerisations compared to conventional statistical copolymerisations using analogous low molar mass monomers (styrene). N-(vinylbenzyl)pyrrolidone is a novel monomer and was synthesised to overcome the problems of the copolymerisation of vinylpyrrolidone with styrene. VBP allows near ideal copolymerisation behaviour with styrene, thus allowing greater control of the copolymer composition. The graft copolymers were subsequently used as stabilisers in dispersion polymerisations of methyl methacrylate, styrene, vinyl pyridine and bis(hydroxyethyl) terephthalate.

Work was initiated on the micellisation behaviour of these preformed graft copolymers in different dispersion media. Kratochvil\textsuperscript{15} has reviewed the work on micellisation of block and graft copolymers. The graft copolymers used previously were of a less well defined structure, this prevented an assessment
of the relationship between micellar structure and chain architecture. By using well defined graft copolymers in the present work, a more detailed study of micellisation behaviour has been carried out. Micellar structures in cyclohexane and toluene were formed with the backbones forming the core and the soluble PS grafts providing stabilisation. Novel micellar structures in methanol were formed which was a non-solvent for the grafts with the backbone component being soluble providing stabilisation by means of loops and tails. Detailed studies were performed to determine the micelle core size and structure and the conformation of the various copolymer components.

Dispersion polymerisation of addition polymers as stated before has been widely reported. The theory of dispersion polymerisation is only qualitatively understood. Most of the detailed work using well-defined stabilisers is based on block copolymers\textsuperscript{16,17}. Very little work has been done on the influence of graft copolymer structure and architecture on the final polymer particle size, shape and stability\textsuperscript{18}. Three different dispersion polymerisations were studied: PMMA/cyclohexane, poly(VP)/toluene and PS/methanol. The use of graft copolymers in which the anchor component is the graft and the soluble backbone is the stabilising segment has not been documented before. A number of parameters were varied in each case to study their influence on particle size, shape and stability.
2. THEORY

2.1 THE THEORY OF STERIC STABILISATION

For a dispersion of polymer particles in a liquid media to remain as discrete particles and not flocculate, the forces attracting the particles to each other must be outweighed by repulsive forces. For polymer particles in aqueous media, ionic surfactants have been adsorbed on to the surface, thereby conferring stability. In organic media, (media of low polarity) this mechanism is not viable. One solution to the problem has been to use "dissolved" polymer chains attached to the surface of the particles as a barrier against flocculation. This principle is termed "Steric Stabilisation".

2.1.1 The forces of attraction

The forces of attraction between two adjacent particles is usually referred to as Van der Waals forces. Three types of such intermolecular attraction are recognised, to explain non-ideal gas behaviour. The first model concerns the interaction of permanent dipoles in separate molecules, which mutually orientate themselves to each other so that attraction results. The second source of attraction predicts that a dipolar molecule will induce dipoles in other molecules, these would be in the correct orientation to cause attraction. Neither of these models account for the attraction of non-polar particles. London\textsuperscript{19} showed that the attraction between two inert gas molecules was a quantum mechanical effect. The Heisenberg uncertainty principle requires that their must be random fluctuations in the electric field. These fluctuations can be considered transient dipoles and therefore induce dipoles in surrounding particles resulting in a force of attraction.

In non-polar materials, London forces account for nearly all of the Van der Waals attraction. The London attractive
potential energy \( V_A \) between two molecules is short range and decreases with the distance of separation \( r \).

\[
V_A = -\frac{L}{r^6}
\]  \hspace{1cm} (2.1)

where \( L \) is the London interaction constant.

Hamaker\textsuperscript{20} showed that the above model for a gaseous system could be applied to condensed bodies in a vacuum, by summing all attractions between the interparticle molecule pairs.

\[
V_A = A \cdot H
\]  \hspace{1cm} (2.2)

where \( A \) is the Hamaker constant and \( H \) a geometrical function.

The Hamaker integration predicts that attraction should occur over distances of several tens of nanometres between particles. However Overbeek\textsuperscript{21} recognised that the electromagnetic interaction is not instantaneous but proceeds at a finite speed, the speed of light. The distance between fluctuating dipoles is greater than the wavelength of the fluctuation frequency. Therefore, dipole oscillations will be out of phase leading to a reduction in attractive energy. This is known as the "retardation effect".

Further modification of the Hamaker approach is required where the condensed particles are within a dispersion medium. The presence of a dispersion media reduces the attractive forces in two ways. The primary effect describes the behaviour of the liquid medium on the transmission of the London field which depends on the dielectric constant for the medium. The secondary effect involves the finite attraction of the particles for the medium. This depends upon the difference between the energy required to separate two particle-medium pairs and the energy released by the formation of particle-particle and medium-medium pairs.

The Hamaker model is based on the interaction of microscopic elements, upon scaling up to macroscopic systems errors are incurred. An alternative approach employed by Lifshitz\textsuperscript{22,23}, in which both the interacting particles and the intervening medium
are treated as a continuous phase. Modifications for retardation and medium effects are no longer required. However, the mathematical treatment is complex and the Hamaker approach still finds widespread use, despite fundamental defects.

2.1.2 The Stabilisation of Colloidal Particles against Flocculation

In the absence of any mechanism to prevent colloidal particles interacting with each other flocculation would rapidly occur. Colloidal stability is achieved in aqueous systems generally by electrostatic charge repulsion, and quantitative theories have been developed based on the Derjaguin-Landau-Verwey-Overbeek (DLVO) theory$$^{24,25}$$.

For colloids in non-aqueous media, the dispersion medium is generally non-ionising and a different mechanism of stabilisation is required. Stabilisation is achieved by surrounding the particles with a surface layer of soluble polymer; this mechanism is generally known as steric stabilisation$$^{26}$$.

As two surfaces, each covered with a layer of soluble polymer, approach each other to a distance less than the combined thickness of the polymer layers (as depicted in figure 2.1(a)) they will interact. An adsorbed polymeric stabilising chain, as shown in figure 2.1(b) may be attached to the particle surface in a number of configurations at one or more points. It is assumed that the stabilising chains are firmly anchored to the particle surfaces, allowing the concept of constant adsorption, where the fraction of segments adsorbed on the surface remains constant. When the particles approach each other, the stabilising chains (i.e. the loops and tails) can redistribute themselves during contact but there is no desorption of the trains. The steric interaction between adsorbed polymer layers produces a change in the Gibbs free energy ($\Delta G$) given by:

$$\Delta G = \Delta H - T\Delta S$$  \hspace{1cm} (2.3)
FIGURE 2.1

(a) SCHEMATIC REPRESENTATION OF STERIC STABILISATION

(b) POSSIBLE CONFIGURATIONS OF ADSORBED POLYMERS
where $\Delta H$ is the change in enthalpy and $\Delta S$ is the change in entropy.

If $\Delta G$ is negative, flocculation will occur but if $\Delta G$ is positive, stabilisation will result. The steric interactions can be divided into entropic and mixing interactions\(^2\(^6\). The adsorbed polymer chains may be compressed without penetrating into one another (see figure 2.2(a)). The 'denting' will reduce the number of possible conformations of the polymer chains, resulting in a decrease in entropy and an increase in free energy ($\Delta G_{VR}$). The interpenetration of adsorbed polymer chains (see figure 2.2(b)) produces a local increase in the concentration polymer segments. This produces an osmotic pressure and an increase in free energy ($\Delta G_M$). Solvent for the stabilising chains diffuses into the regions of high polymer concentration forcing the particles apart. This is termed the osmotic, mixing or enthalpic effect\(^2\(^6\). The total interaction free energy ($\Delta G_T$) between two polymer covered particles is given by

$$\Delta G_T = V_A + V_R + \Delta G_S$$  \hspace{1cm} (2.4)

where $V_A$ is the attractive potential energy, $V_R$ is the repulsive potential energy and $\Delta G_S$ is the total steric interaction. It is assumed that the entropic and mixing contributions are additive for $\Delta G_S$.

The variation of net potential energy with interparticle distance, for a dispersion of particles stabilised with a soluble polymer layer in a good solvent is shown in figure 2.3(a). It can be seen that the repulsive energies are only generated when the soluble polymer chains interact, this is fundamental to the concept of steric stabilisation. As overlap of polymer chains occurs when the particles approach each other, the repulsive potential energy exceeds the attractive potential energy. Therefore, the net repulsive energy is always positive and increases rapidly as the separation of particles decreases. In some cases, the layer thickness and particle size
FIGURE 2.2
THE INTERACTION BETWEEN ADSORBED POLYMERs ON STERICALLY STABILISED PARTICLES

(a) ENTROPIC INTERACTIONS

(b) MIXING INTERACTIONS
FIGURE 2.3
THE FORM OF NET POTENTIAL ENERGY CURVES AS A FUNCTION OF PARTICLE SURFACE SEPARATION (d) FOR STERIC STABILISATION

(a) LARGE ADSORBED LAYER THICKNESS
(b) SMALL ADSORBED LAYER THICKNESS
may give rise to a significant attractive force, thus producing weak flocculation due to a secondary minimum \( (V_{\text{min}}) \). This is illustrated in figure 2.3(b). If the steric barrier is relatively small, then \( V_{\text{min}} \) increases appreciably. \( V_{\text{min}} \) plays an important role in controlling the stability and flocculation behaviour of sterically stabilised dispersions.

The question of whether entropic or mixing interaction predominate will depend on a number of factors. At small separations, compression should predominate but at separations greater than one layer thickness interpenetration is most likely to occur. There will also be a dependence on segment density, if this is high then compression will be favoured.

2.1.2.1 Models for Steric Stabilisation

Mackor\(^\text{27}\) was the first to model entropic interactions between sterically stabilised particles. He proposed a model in which the polymer chains were represented by rigid rods, attached flexibly at one end to a flat surface. It was shown that the total number of possible conformations of the stabilising chains when two particles approached one another decreased thus resulting in repulsion. However, the model assumed that the stabilising chains were volumeless. Mutual interactions were ignored, therefore, the theory only applied to small surface coverages. Subsequently, these interactions were accounted for by introducing a lattice model for the adsorbed polymer and the medium\(^\text{28}\). The model was still limited to dilute solutions though. A quantitative treatment of the entropic repulsion mechanism using Monte Carlo computer simulation methods was proposed using terminally adsorbed homopolymers on a cubic lattice as a model\(^\text{29}\). Additionally, the flexibility of the polymer chains was considered using random flight chains and the excluded volume effect. Clayfield and Lumb also allowed for solvent interactions\(^\text{30}\) and extended their model to statistical copolymers with a loop-type adsorption\(^\text{31}\). However, in all these cases, no interpenetration interactions were accounted for.
Fischer first proposed a theory to quantify mixing interactions in steric stabilisation. In calculating $\Delta G_M$, Fischer considered the overlap of polymer layers attached to two spherical particles. He assumed that the segment concentration was uniform in each adsorbed layer and in the overlap region was the sum of the individual segment concentrations of the adsorbed layers. Also the free energy of mixing of the adsorbed layers was assumed to equal the free energy of mixing for a dilute polymer solution (Flory-Krigbaum theory). Fischer derived an expression of the form

$$\Delta G = A \cdot B$$

where $A$ is the geometric term and $B$ is the thermodynamic term, i.e. the second virial coefficient of the polymer in solution. $B$ is proportional to $(0.5 - \chi)$ where $\chi$ is the polymer-solvent interaction parameter. An important controlling factor for $\Delta G_M$ is the thermodynamic state of the solvent for the stabilising chains. Similar expressions have also been derived by Ottewill and Walker and Napper. The drawbacks of the Fischer model are that the polymer segment concentration is uniform and that the redistribution of polymer segments in the overlap region is ignored. Both assumptions lead to an over estimation of the repulsive forces particularly in the initial stages of interaction.

So far the models have considered the entropic or mixing terms in isolation. However, as stated earlier both effects are likely to occur. Meier was the first to publish a combined theory based on random flight statistics for the stabilising molecules adsorbed terminally to planar surfaces. Further modification to include loops for homopolymers, where all segments had an equal probability to become adsorbed at the interface. Meier and Hesselink et al calculated the entropic and mixing terms separately and then assumed that the total steric interaction was the sum of the two contributions. Dolan and Edwards pointed out that these terms were interdependent. They avoided the separate treatment of the entropy and mixing.
terms by treating the interactions between segments as an excluded volume effect, thereby including the whole free energy as a configurational entropy term. This self-consistent mean field theory was further developed by Scheutjens and Fleer for polymers at interfaces\textsuperscript{39,40}. The model described the adsorption of homopolymers from solution at one interface. This interface was represented by a flat surface and the polymer solution was represented by a lattice of various geometries with lattice sites occupied by either polymer segments or solvent molecules (see figure 2.4). Segmental weighting factors were used to determine the probability of a given conformation. The factors described the energy and entropy changes that occurred when a polymer segment moved from bulk solution to its position in the lattice. By use of matrix procedures it was possible to generate all conformations and from the conformational probabilities, a segment concentration profile was calculated by summing over all probabilities. It was assumed that all sites within one layer parallel to the surface were equivalent. Further modifications extended its use to homopolymers between two surfaces\textsuperscript{41,42} applicable to colloid stability. Recently, the theory has been applied to the structure of grafted polymer and copolymer molecules at interfaces\textsuperscript{43}. The major advantages of this model is that it can be applied to any type of copolymer because the ranking number of each segment is taken into account.

Scaling theories have also been applied to the behaviour of polymers at interfaces. Dilute polymer solutions with overlapping coils are represented by an idealised grid\textsuperscript{44} (see figure 2.5(a)). The mesh size of the grid decreases as the volume fraction of polymer increases. De Gennes\textsuperscript{44} suggests that for a polymer adsorbed at an interface, the local mesh size at any distance $Z$ from the interface is equal to $Z$ itself, i.e. the layer of polymer has a 'self-similar grid structure' see figure 2.5(b). These scaling theories have been developed to describe grafted chains between two surfaces\textsuperscript{45}.
FIGURE 2.4
A LATTICE MODEL FOR ADSORBED POLYMER CHAINS WITH TWO POSSIBLE CONFORMATIONAL STATES FOR A CHAIN WITH 14 SEGMENTS AND 13 BONDS

interface

0 = segment

= bond
FIGURE 2.5

(a) A POLYMER SOLUTION (VOLUME FRACTION $\phi$) IDEALISED AS A "GRID" WITH THE SAME MESH SIZE, ($\xi$)

(b) AN ADSORBED POLYMER LAYER REPRESENTED AS A "SELF-SIMILAR GRID". AT ANY DISTANCE, $Z$, FROM THE WALL, THE LOCAL MESH SIZE EQUAL TO $Z$.
Much discussion has surrounded the applicability of these theories to the behaviour of polymers at interfaces. The 'mean field' theory states that the segment density is essentially homogeneous parallel to the particle surface. De Gennes argues that adsorbed layers are strongly fluctuating systems and this approximation is incorrect. This is probably true for conditions of low overlap and scaling theories are probably more appropriate. Scaling theories are generally only applicable for dilute solutions and that for situations where adsorbed layers interact, the concentration is too high for scaling laws to apply. These two theories in combination describe many of the characteristics of macromolecules at interfaces and the interactions between them.

2.1.3 The Stability and Flocculation of Colloidal Dispersions

It is essential that during particle collision there is no relieving of repulsive force involved in sterically stabilised dispersions. A number of criteria need to be fulfilled for a dispersion stabilised by adsorbed polymer to remain stable. First, firm anchoring of the stabilising chains to the particle surface in order to prevent desorption and lateral movement on the particle surface. The particle surface must be completely covered by stabilising chains. The steric barrier must be thick enough so that $V_{\text{min}}$ is negligibly small. Lastly the dispersion medium should be a thermodynamically good solvent for the stabilising chains.

Instability can be induced in sterically stabilised dispersions by reducing the solvency of the dispersion medium for the stabilising chains, either through temperature changes or the addition of a non-solvent. Under such conditions, dispersions often exhibit rapid flocculation. There is a strong correlation between critical flocculation point and the $\Theta$-point of the stabilising chains in free solution. It should be noted that although $\Theta$-conditions are independent of molar mass, there may be a deviation at very low molar masses from this
behaviour. $\theta$-conditions may also differ for a terminally adsorbed polymer chain at an interface.

2.2 **DISPERSION POLYMERISATION IN NON-AQUEOUS MEDIA**

Most types of polymerisation can be performed as dispersion polymerisations. These can be based on free radical and ionic addition, condensation and ring-opening mechanisms. The mechanism and kinetics of dispersion polymerisation have largely been derived from studies of radically polymerising systems.

2.2.1 **A Comparison of Heterogeneous Polymerisation Processes**

Several heterogeneous polymerisation techniques have been developed. The various techniques can be divided into two types. Firstly, those which are heterogeneous throughout the polymerisation, and those which are initially homogeneous until polymer precipitates and the reaction continues in a heterogeneous manner.

Emulsion polymerisation is characterised by low monomer solubility in the reaction medium (water) and an initiator which is soluble in the aqueous phase. Ionic or non-ionic surfactants are also used. A high rate of polymerisation and high molar mass product is produced owing to radical isolation within the particles. The latex particles produced are typically 0.1-0.3μm diameter.

Suspension polymerisation is a somewhat similar technique except the initiator are soluble in the monomer. Lower levels of surfactant are required and polymerisation occurs within the suspended monomer droplets in a "micro-bulk" fashion. The particles produced are coarser than those from emulsion polymerisation, typically greater than 5μm.

Precipitation polymerisation is initially homogeneous, the monomer and initiator soluble in the diluent. The polymer precipitates as a coarse agglomerate or slurry. This process is usually characterised by an auto-acceleration effect as a
result of radical trapping within the highly viscous precipitated polymer.

Dispersion polymerisation may be regarded as a special case of precipitation polymerisation in which the precipitating polymer particles are prevented from flocculation, thereby controlling particle size. A typical dispersion polymerisation begins with a homogeneous solution of monomer, initiator and macromolecular stabiliser in a diluent (which is generally non-aqueous). As monomer is polymerised the insoluble polymer precipitates as discrete particles which are prevented from flocculation by the adsorption of the stabiliser. Polymerisation proceeds within the monomer-swollen particles and often auto-acceleration is observed. Particle sizes obtained are typically in the range of 0.05-10 \( \mu m \).

2.2.2 The Role of the Stabiliser

The function of the stabiliser is to provide a layer of polymer chains solvated by the dispersion medium on each particle surface. The steric barrier should be firmly anchored and thick enough to prevent flocculation. Homopolymers and statistical copolymers generally are not suitable for steric stabilisation. Homopolymers containing groups that anchor strongly to the particle surface will adopt a flat conformation mostly in trains. Alternatively, if the homopolymer has a stronger affinity for the dispersion medium then only weak adsorption on the particle surface will occur, thus allowing easy displacement from the surface. Statistical copolymers in rare cases can provide a suitable steric barrier if the correct balance of anchoring groups is found. The most successful stabilisers are those based on block and graft copolymers consisting of two components, one soluble and the other insoluble in the dispersion medium\(^3,4\). The stabilising copolymer is firmly attached by its insoluble component (anchor block, A) to the particle surface owing to its insolubility in the dispersion medium. The soluble component, B is chosen to have little or no affinity for the particle surface and
therefore extends into the dispersion medium to provide a stabilising barrier. The effectiveness of the stabiliser can be enhanced if the anchor block is compatible with the dispersed phase\(^3\). Anchoring of such stabilisers is achieved by a physical adsorption mechanism (see figure 2.6(a)). Alternative methods for the anchoring polymeric stabilisers include acid-base interactions and covalent links\(^{48,49}\). These methods of anchoring are useful under conditions of high temperature.

Figure 2.6(b) shows some possible configurations which may be effective steric stabilisers. The present study concerns the use of graft copolymers of type (1) and (4). Such copolymers can be produced 'in situ' during dispersion polymerisation from a precursor, although graft copolymer structures maybe difficult to characterise and control\(^{50}\).

2.2.3 The Behaviour of Stabilisers in Solution

Amphipathic block or graft copolymers, consisting of polymer segments with different chemical compositions are capable of forming aggregates in solution. The solvent has to be selectively poor for one of the chain segments\(^{51}\). The morphology obtained depends upon the concentration and composition of the copolymer, the solvent environment and the temperature. The formation of these aggregates is analogous to the micellar structures observed in aqueous ionic surfactant solutions.

In a solution of such a copolymer there are strong interactions between the solvent and the copolymer that result in the expulsion of the selectively poor component. This produces the tendency for the aggregation of the copolymer to form micelles (see figure 2.7). The free energy of the selectively poor component decreases while the well solvated component increases. As a consequence of the reduction of the interfacial area between the selectively poor component and the solvent the total free energy is also reduced. The driving force for micellar formation is the reduction of the total free
FIGURE 2.6

(a) GRAFT AND BLOCK COPOLYMERS USED AS STERIC STABILISERS

![Diagram of graft and block copolymers]

(b) SUITABLE COMBINATIONS OF A AND B
FOR USE AS COPOLYMER STABILISERS

![Diagram of suitable combinations of A and B combinations for copolymer stabilisers]
FIGURE 2.7
THE BEHAVIOUR OF GRAFT COPOLYMERS IN A SELECTIVE SOLVENT
(NONSOLUBLE FOR THE BACKBONE)
energy. The shape and size of the micelles produced is therefore determined by the minimalisation of the free energy.

At very low concentrations, copolymer molecules will exist in an unassociated manner as in a conventional homopolymer solution. This is below the critical micelle concentration (CMC). At or above the CMC, the copolymer molecules aggregate to give a micelle in which the core is composed of the least soluble component of the copolymer. The critical micelle concentration for an ionic surfactant in water is of the order $10^{-3}$ mol.L$^{-1}$, for a non-ionic surfactant it is $10^{-4}$ mol.L$^{-1}$. The CMC is related to the thermodynamics of micelle formation. Price$^{51}$ has shown that for block and graft copolymers in organic solvents the free energy of micellisation is determined by the enthalpic contribution, the entropy of micellisation is negative as predicted by statistical arguments. The enthalpic term is largely due to the exothermic interchange energy accompanying the replacement of polymer-solvent interactions with polymer-polymer and solvent-solvent interactions on micelle formation. For synthetic surfactants in water, the entropy contribution determines the free energy change for micellisation. The entropy term is negative due to structural changes which occur in the water matrix when the hydrocarbon chains are withdrawn to form micellar cores$^{52}$.

At higher concentrations (>20%) these aggregates coalesce into regular and periodic structures of three main types: spheres, rods or cylinders, and lamellae$^{53}$. Price et al$^{54}$ have shown the existence of 'worm-like' micelles. They studied a polystyrene-b-polyisoprene block copolymer in N,N'-dimethylacetamide. The micelles were metastable, on heating they reverted to spherical micelles. The formation of these worm-like micelles was shown to be dependent on the thermal history, concentration, molar mass of the copolymer and its composition.

Dispersion polymerisation usually involves copolymer stabilisers at a concentration of a few per cent. The dispersion medium is a selective solvent for the one of the
copolymers components. The size of the micelle formed depends largely upon the ratio of the anchor and stabiliser components. The concept of anchor/soluble balance (ASB) was introduced analogous to hydrophile/lipophile balance (HLB) for emulsifiers. At ASB values close to unity, block and graft copolymers at a few percent concentrations aggregate to form micelles in equilibrium with free copolymer molecules and adsorbed stabiliser as shown in figure 2.8. It has been proposed that monomolecular micelles are composed of a collapsed core of the insoluble component surrounded by a layer of soluble component.\(^{55}\)

When the ASB ratio is small (i.e. the anchor block is small), the copolymer will exist mainly as monomolecular micelles and will not be preferentially adsorbed onto the particle surface. If the ASB ratio is large the copolymer molecules will favour multimolecular micelles and therefore will inhibit dissociation into monomolecular micelles, thereby preventing adsorption of stabiliser onto the particle surface. If the ASB ratio is even higher, then the stabiliser will not even form stable micelles because it becomes impossible to surround the insoluble component with a layer of soluble stabilising chains. It has been suggested that the ASB ratio should be in the range of 1:3 to 3:1.\(^{56}\)

The size of micelles formed is predicted to increase as the cube root of the degree of polymerisation of the copolymer.\(^{57}\) The size will increase as the interfacial energy per unit area between the core and the solvated outer layer becomes larger. Therefore, larger micelles will be formed as the incompatibility of A and B increases. Steric stabilisation of micelles prevents micelles combining (i.e. the total free energy is minimised).

It is possible to calculate the number of copolymer molecules required to form a continuous layer of soluble polymer around the insoluble core.\(^{4}\) The micellisation number, \(n\) is given by
FIGURE 2.8
THE BEHAVIOUR OF GRAFT COPOLYMERS IN DISPERSION POLYMERISATION

STABILIZED PARTICLE

UNASSOCIATED
GRAFT COPOLYMER

GRAFT COPOLYMER
MICELLE
where $M_A$ is the molar mass of the insoluble chains, $C$ is the surface area (area stabilised by one soluble chain), $x$ is the number of soluble chains attached to each insoluble chain, $p$ is the density of the particle core (assumed), $n$ is the number of copolymer molecules per micelle.

The micelle core radius is given by

\[
n = \frac{36\pi}{(0.6023)^2} \left( \frac{M_A}{\rho} \right)^2 \frac{1}{C^3 x^3}
\]  

(2.6)

2.2.4 The Mechanism of Particle Formation

Initially, as in conventional free radical solution polymerisation, the initiator breaks down to generate free radicals which react with the monomer to form growing oligomeric chains in a homogeneous solution. These chains continue to grow until a threshold molar mass is reached, at which point the polymer precipitates and forms particle nuclei. Three different models have been proposed for the formation of particle nuclei. Self-nucleation, aggregative nucleation and nucleation from micelles are shown in figure 2.9.

2.2.4.1 Self-nucleation

A polymer chain grows in solution until it reaches a threshold molar mass at which point it collapses into a condensed state and forms a particle nucleus. The threshold molar mass will be dependent upon the solvency of the dispersion medium. The growing chain will form a new nucleus
FIGURE 2.9
MODELS FOR PARTICLE NUCLEATION IN DISPERSION POLYMERISATION

Primary radicals

Initiation and growth of oligomers

(a) * → O

Self-nucleation

(b) * → O → O

Aggregative nucleation

(c) * → O → O

Nucleation from monomer-swollen micelles of surfactant
unless it is captured by diffusion into a particle before it reaches the threshold molar mass.

2.2.4.2. **Aggregative-nucleation**

The growing polymer chains associate with each other as their molar mass and concentration increase. These aggregates are unstable until a critical threshold molar mass and concentration is reached at which point they are irreversibly associated and become a particle nucleus. The rate of nucleation depends on the activation energy required to form an aggregate of critical size. Again, capture of existing growing chains competes with nucleation.

2.2.4.3 **Nucleation from micelles**

As discussed previously block or graft copolymers used as stabilisers are capable of forming micelles in the dispersion medium. It is suggested that the chains are initiated and grow within the monomer-swollen micelles until a critical molar mass is reached when a nucleus is formed. This idea is analogous to the model proposed by Harkins for emulsion polymerisation. The monomer in dispersion polymerisation is completely soluble in the dispersion medium, therefore Harkins model is thought unlikely. The other two models are thought to be complimentary, with a bias towards one mechanism depending upon monomer solubility, polymerisation rates etc.

If polymer solubility is very low in the dispersion medium, self-nucleation of individual polymer chains is likely to occur. Alternatively, if polymer solubility is high then the concentration of polymer is also high before a critical threshold molar mass is reached, therefore aggregative nucleation is likely. In the absence of any competing processes, the formation of nuclei would continue unabated throughout the polymerisation process. In reality, the rate of nucleation drops to a low level in the early stages of polymerisation, because nearly all the growing polymer chains
are captured by existing particles before their critical threshold molar mass is reached.

The above models for nucleation do not include the influence of stabilisers. The presence of a stabiliser generally enhances nuclei formation, because of the association of stabiliser molecules with growing polymer chains. This increases the probability of nucleation and reduces the probability of capture by existing particles. In the self-nucleation model, the stabiliser associates with a single growing chain as shown in figure 2.10(a). In the aggregative nucleation model, (figure 2,10(b)), the stabiliser participates in the formation of incipient nuclei and reduces the total free energy.

2.2.5 The Mechanism of Particle Growth

If the reaction conditions remain unchanged, most of the nuclei are formed early in the polymerisation. Following nucleation, subsequent polymerisation is largely confined to further growth of existing polymer particles. Three mechanisms have been proposed to explain particle growth. The first mechanism proposes that polymerisation occurs within solution, followed by precipitation onto existing polymer particles. Alternatively, polymerisation occurs at the interface of the particle surface of adsorbed monomer. Finally, polymerisation takes place inside the polymer particle with adsorbed monomer.

From a study of dispersion polymerisation of methyl methacrylate in n-dodecane, a number of features were evident. Firstly, as stated previously, the rate of dispersion polymerisation was found to be higher than an equivalent solution polymerisation. This is a result of the auto-acceleration effect, and indicates that polymerisation occurs mainly within the polymer particles. Secondly, the rate of dispersion polymerisation is unaffected by particle size, indicating that a surface polymerisation mechanism is improbable. This suggests, that the last mechanism is the predominant mode of polymerisation.
FIGURE 2.10
THE EFFECT OF STABILISER ON THE MODIFICATION OF PARTICLE NUCLEATION IN DISPERSION POLYMERISATION

(a) Self-nucleation

(b) Agregative-nucleation
2.3 DISPERSION POLYMERISATION OF CONDENSATION POLYMERS

Stable dispersions of condensation polymers can be produced by the direct dispersion polymerisation of soluble reactants in organic media in the presence of a polymeric stabiliser\(^61,62\), usually a graft copolymer. The process is analogous to the free radical dispersion polymerisation with the exception that the growth of the polymer occurs in a step-wise fashion leading to a slow, multiple build-up in molar mass with a sudden, large requirement for polymeric surfactant when the condensation polymer becomes insoluble in the dispersion medium. This method has been used for the reaction of diacid chlorides with diols.

In most cases though, the condensation polymer precursors are not soluble in the dispersion medium. It is usual to use an emulsion of a monomer for the subsequent polymerisation in a dispersion. In such cases, the graft copolymer stabiliser must also act as an emulsifying agent. Nicks and Osborne\(^63\) have directly emulsified a liquid reactant into fine droplets in the organic diluent with the use of a graft copolymer stabiliser. In contrast to conventional dispersion polymerisations where particles are formed as the polymerisation proceeds, the initial emulsion droplets largely determine the particle size of the condensation polymer. Their size depends not only on the level and nature of the graft copolymer used but also on the overall efficiency of the emulsification process.

The dispersion medium must not contain any groups which may interfere with the condensation polymerisation. In general, this narrows the choice to aliphatic or aromatic hydrocarbons. These must also be high boiling to allow azeotropic distillation of by products (usually water or alcohols). As the dispersion medium has a low viscosity this allows the by-product to be removed with greater ease compared to bulk polymerisation. Dispersion polymerisations of condensation polymers are generally carried out some 50-70°C below the normal bulk polymerisation temperature.
A typical method for a dispersion of poly(ethylene terephthalate) is: an emulsion of bis(hydroxyethyl) terephthalate in a high boiling petrol (240-250°C) with a graft copolymer stabiliser consisting of poly(methyl methacrylate) backbone with grafts of poly(12-hydroxystearic acid), followed by azeotropic distillation of ethylene glycol to give poly(ethylene terephthalate). Particle size varies between 1-50μm, with a wide particle size distribution. The mechanism for polymerisation may be more akin to suspension polymerisation.

2.4 THE SYNTHESIS OF GRAFT COPOLYMERS

Graft copolymers have branched molecular structures. They are composed of a linear main chain (the backbone), to which are attached polymeric side chains (the grafts), these are generally randomly distributed. The simplest representation of a graft copolymer is:

```
AAAAAA....BB.BBBB.B.B
B    B    B    B
B    B    B    B
B    B    B    B
```

There are three major methods used in graft copolymer synthesis: 'grafting from', 'grafting onto' and 'grafting through'. These are well documented in several reviews.8,64

2.4.1 Grafting-from Processes8,64

A polymer chain may have initiating sites, or functions capable of generating such sites. These sites can then be used to initiate the polymerisation of a second monomer to form the grafts, provided that initiation occurs by addition to the incoming monomer, as in figure 2.11(a).

This method was originally developed in the 1950's by Smets et al65 and Bamford et al66. These methods are quite efficient, but no accurate knowledge of the molecular structure of the graft copolymer formed is provided. It is not possible to
FIGURE 2.11
COMPARISON OF METHODS USED TO SYNTHESIZE GRAFT COPOLYMERS

(i) "GRAFTING FROM" PROCESS

\[
\begin{align*}
\{ & * + nCH_2=CHR \rightarrow CH_2-CHR-CH_2-CHR\ldots \\
\{ \\
\}
\end{align*}
\]

where \( * \) = active site

(ii) "GRAFTING ONTO" PROCESS

\[
\{ \}
\begin{align*}
\{ & -X + Y-CH_2-CHR\ldots \rightarrow \square-CH_2-CHR\ldots \\
\{ \\
\}
\end{align*}
\]

(iii) "GRAFTING THROUGH" PROCESS

\[
\{ \}
\begin{align*}
\{ & CH_2 \\
\{ & \square-CHR-CH_2\ldots \rightarrow \square-CH_2-CHR-CH_2\ldots \\
\{ & \square \\
\}
\end{align*}
\]
determine the number of grafts experimentally, and their length may fluctuate widely within a given sample. The other major disadvantage is the amount of both homopolymers formed in the graft copolymer.

2.4.2 Grafting-onto Processes\(^8,64\)

Grafting-onto results from the reaction between a polymer molecule carrying one reactive site at a chain end, and another polymer with attached functional groups distributed randomly along its chain (see figure 2.11(b)). This type of grafting reaction does not involve a chain reaction; this does not imply that access to the grafting sites is always possible. Owing to the incompatibility between some polymers of different chemical natures, a common solvent is required to provide homogeneity of the reaction medium. One major advantage of this method is that structural determination of the graft copolymers formed is possible, because the backbone chain and grafts can be characterised separately before grafting. It is therefore possible to calculate the number of grafts per chain, and the average distance between two successive grafts. Azam\(^67\) has recently described the synthesis of a number of polyethylene based graft copolymers using a grafting-onto method.

2.4.3 Grafting-through Processes\(^8,64\)

The polymerisation of a monomer in the presence of a polymer carrying pendant unsaturated groups will result in grafting (see figure 2.11(c)). However, if a growing site happens to incorporate unsaturation from two different backbones, then crosslinking will occur.

2.4.4 Copolymerisation of Macromonomers

The preparation of graft copolymers from macromonomer precursors is a relatively new innovation which has attracted much interest in recent years\(^8,9,10\)

Macromonomers are defined as linear macromolecules carrying at their chain end some polymerisable function. They can also
be bifunctional carrying an active double bond at each end of their chain; this will result in network formation. Copolymerisation of this species with a suitable comonomer allows access to well defined graft copolymers (see figure 2.12). As the macromonomer is made separately, it can be characterized independently. The backbone chain is formed upon copolymerisation, usually by free radical methods. It is possible for the length and number of grafts to be varied by altering the molar mass of the macromonomer and its initial concentration in the copolymerisation. It is possible to prepare a variety of graft copolymers with a well-defined structure and composition containing very little backbone homopolymer contamination by this method. The copolymerisation of macromonomer is a modified grafting-through process.

2.4.5 Miscellaneous Methods

There are a number of other ways of synthesising graft copolymers which do not fall into the three above categories. Grafting can occur from the result of ionising radiation on a polymer in the presence of a monomer. Radical sites are formed which initiate the growth of the grafts. Transfer reactions have also been used for grafting. Some polymers exhibit high transfer constants, and therefore when the polymerisation of a monomer is carried out in the presence of a polymer, radical sites are formed on the backbone. These can initiate the polymerisation of the monomer to build a graft. However, the low grafting efficiency and homopolymer contamination are disadvantages. This is covered in more detail elsewhere.

2.5 SYNTHESIS OF MACROMONOMERS

Macromonomer synthesis has been well-documented in three reviews. Anionic, cationic and free-radical polymerisation techniques are the most common methods used, with a few examples of polyaddition and group transfer processes.
FIGURE 2.12
SCHEMATIC REPRESENTATION OF THE FORMATION OF GRAFT COPOLYMERS FROM THE FREE-RADICAL COPOLYMERISATION OF MACROMONOMERS

macromonomer

solvent
initiator
heat

comonomer

graft copolymer
2.5.1 Anionic Polymerisation

Anionic polymerisation can be traced back to the end of the last century, although it was not until the late 1940's that the mechanisms involved were elucidated. The first patent appeared in 1910 and was issued to Matthews and Strange, this described the polymerisation of dienes induced by alkali metals. Schlenk, four years later described the formation of high molar mass polymers in ether solution by reacting styrene with sodium dust. It was not until 1920 that the chain character of addition polymerisation was recognised by Staudinger.

Sanderson and Hauser postulated an anionic mechanism for the polymerisation of styrene initiated by sodamide in liquid ammonia. Addition of \( \text{NH}_2^- \) to the \( \text{C} = \text{C} \) double bond was assumed to initiate the chain process. Chain transfer of a proton from ammonia to the growing carbanion regenerated the initiating species.

Szwarc and his coworkers reported the termination-free polymerisation of vinyl monomers and were the first to appreciate and demonstrate the potential of such systems. It was shown that it was possible to initiate the polymerisation of styrene using a sodium/naphthalene complex formed in the presence of tetrahydrofuran (THF) under extreme conditions of purity. In the absence of any terminating agents, even when all the monomer had been consumed, the red solution of polystyryl sodium still contained active chain ends. It was shown that this activity remained almost indefinitely; when further monomer was added, further polymerisation took place. The phrase 'living polymers' has been coined, although the anions formed are not immortal and can be killed off by spontaneous termination over a long period of time.

In a suitable solvent such anionic polymerisations proceed with little chain transfer and are devoid of a spontaneous termination step. However, these systems are very susceptible to termination by impurities able to donate protons such as...
water and alcohols. When termination-free systems are obtained the following control in the synthesis of polymers is possible:

(1) Synthesis of polymers having a predictable molar mass average, from simple stoichiometry.

(2) Very narrow molar mass distributions, approaching the Poisson type, by proper adjustment of initiation versus propagation kinetics.

(3) Synthesis of true block copolymers by sequential addition of different monomers to the living polymer chains.

(4) Formation of polymers with functional end groups by selective termination with appropriate reagents.

Each molecule of a monofunctional initiator is capable of initiating one polymer chain and thus the desired molar mass polymer may be prepared by varying the ratio of monomer to initiator. A monofunctional initiator will therefore generate a polymer chain with a number average molar mass $M_n$ given by:

$$M_n = \frac{\text{grams of monomer}}{\text{moles of initiator}}$$

Initiators commonly used include alkali metals and their organometallic derivatives. The sodium/naphthalene complex is a bifunctional initiator, as are other alkali metals. Anionic systems and their applicability, including the range of initiators used have been extensively reviewed. As early as 1935 Dostal and Mark, had considered the effect of the rates of initiation and propagation on the molar mass distribution in a nonterminating polymerisation. It was Flory though, who first treated the system quantitatively. He based his treatment on the polymerisation of ethylene oxide by sodium alkoxides, where the rate of initiation step is of the same order of magnitude as that of the propagation step and there is no termination or transfer. At high molar masses, he predicted that a very narrow (Poisson) distribution is found. The molar mass distribution in such a system is defined by:
\[ p_j = e^{-x \frac{x}{j+1}} \frac{1}{(j-1)!} \]
\[ w_j = \left[ \frac{x}{x+1} \right] e^{-x \frac{x}{j+2}} \frac{1}{(j-1)!} \]

where \( p_j \) and \( w_j \) are the number and weight fraction of j-mers and \( x \) denotes the number of monomer units which have reacted per initiator molecule. Hence, the ratio of weight average \( (x_w) \) to number average \( (x_n) \) chain length, is given by

\[ H = \frac{x_w}{x_n} = 1 + \frac{(x_n - 1)}{x_n^2} \]

Therefore, when \( x \) is 100, \( H \) is 1.01, so the polymer is virtually monodisperse. The assumptions made are that (i) there is no termination or transfer during chain growth, (ii) the initiation step is at least as rapid as the propagation, and (iii) all the monomer molecules have an equal probability of reacting (perfect mixing). In practice assumptions (i) and (ii) are possible but perfect mixing is very difficult. Furthermore, experimental measurements do not have sufficient accuracy to determine values as low as 1.01. The lowest values currently measured being between 1.03 and 1.05.

In any ionic system there must be a counter ion to the active species to ensure electrical neutrality. Anionic polymerisation is propagated by macromolecules with reactive end groups (anions) which can exist in a variety of forms; these include; free ions, ion pairs and higher aggregates. In theory all the species contribute to the reaction, each having a different reactivity. Each of these species would have a relative abundance determined by the relevant ionic association and dissociation equilibria. Ionic end groups of the propagating polymer chain can interact with similar groups of other similar chains or with polar or polarisable molecules in the system. Therefore, the formation of dimeric (and higher) anionic complexes are a possibility. Solvent molecules or added substances (e.g. THF) can solvate the anions in the system thus reducing the amount of complexation taking place.
A number of important considerations should be taken into account when trying to synthesise polymers of a predictable and narrowly-distributed molar mass. Firstly, reactions should be carried out in a well stirred homogeneous solution. The choice of initiator is important; an efficient initiator with a rapid rate of initiation is required. Additionally, the initiator should have a suitable counter ion to the growing chain end since this often affects the rate of propagation. The reaction medium will also affect the rates of initiation and propagation by any solvating action of the ions in solution.

2.5.1.1 Styrene Polymerisation

The anionic polymerisation of styrene was the first nonterminating system to be reported and therefore is also the most investigated reaction (see figure 2.13). Morton et al\textsuperscript{81} showed that polystyrene prepared anionically in benzene solutions with n-butyl lithium as an initiator had broader molar mass distributions than expected. This is due to a slow initiation reaction.

It is well known that in hydrocarbon solvents organolithium compounds are highly associated, Margerison and Newport\textsuperscript{82} showed that n-butyl lithium existed almost entirely in a hexameric form. It was proposed as a six membered ring of lithium atoms. The following order of initiation rates for styrene was proposed in hydrocarbon solvents for organolithium compounds in decreasing order of reactivity.

\[ \text{menthyl} > \text{s-butyl} > \text{i-propyl} > \text{n-butyl} \text{ and ethyl} > \text{t-butyl} \]

In hydrocarbon solvents, polystyryl lithium is associated as dimers. Evidence for this was provided by Worsford and Bywater\textsuperscript{83,84} by kinetic studies of the polymerisation. Later they suggested that the propagation step for n-butyl lithium initiated styrene polymerisation in benzene was due to the small concentration of highly reactive free ion pairs in equilibrium with unreactive dimeric ion pairs. These dimers may be broken down by small amounts of ether such as THF. A
FIGURE 2.13
THE REACTION SCHEME FOR THE ANIONIC POLYMERISATION
OF STYRENE TERMINATED WITH AN UNSATURATED DEACTIVATOR

\[
\begin{align*}
\text{CH}_3 & \text{-CH-CH}_2 \text{H} + \text{CH}_2=\text{CH}_2 & \xrightarrow{\text{initiation}} & \text{CH}_3 \text{-CH-CH}_2 \text{-CH-CH}_2 \text{-CH}^+ \text{Li}^+ \\
\text{CH}_3 & \text{-CH-CH}_2 \text{-CH}_2 & \xrightarrow{\text{Propagation}} & \text{R} \text{-OH} \\
\text{CH}_3 & \text{-CH-CH}_2 \text{-CH}_2 & \xrightarrow{\text{termination}} & \text{R} \text{-X} \\
\text{CH}_3 & \text{-CH-CH}_2 & \xrightarrow{\text{+LiX}} & \text{R} = \text{CH}_2 \text{-CH}_2 \text{-CH}^+ \text{Li}^+ \text{or} \text{CH}_2 \text{-C(OCH}_3)_2
\end{align*}
\]
monoetherate of the ion pair with a high reactivity is formed which augments the propagation rate without changing the kinetic order with respect to the initiator. With higher THF concentrations a dietherate is formed which does change the kinetic order with respect to the initiator from 0.5 to 1. The dietherate is less reactive and therefore as the concentration of THF is increased the rate of propagation passes through a maximum. If the THF is added before the monomer, the hexameric n-butyl lithium will break up and therefore lead to more rapid initiation. Altares et al\textsuperscript{85} have observed this by polymerising styrene in benzene solutions with a small amount of THF present to give narrow molar mass distribution samples.

The nature of the ion pairs does depend on the solvent used, e.g. living salts of polystyrene in dioxane form tight ion pairs. The rate of propagation of living polystyrene salts in dioxane does depend on the nature of the counter ion. The reactivity of the $\sim\sim S^- \text{Cat}^+$ pairs increase with the size of the counter ion ($\text{Li}^+<\text{Na}^+<\text{K}^+<\text{Rb}^+<\text{Cs}^+$). This series does not normally apply. In THF the ion pairs are partially dissociated and free carbanions are much more reactive than the ion pairs. Therefore, the trend for the rate of propagation of polystyryl salts in THF is reversed. This can be partly explained by the solvation of the various cations. The radius of Na$^+$ ion in THF is larger than that of Cs$^+$.

The above observations suggest that the structure of an ion pair varies with the nature of the solvent and the counter ion, and probably on concentration.

Toluene has been used as a solvent in some early work, but chain transfer has been acknowledged to take place. Bower and McCormick\textsuperscript{86} and Brooks\textsuperscript{87} have observed chain transfer in the organo-sodium initiated polymerisation of styrene in toluene. Gatzke\textsuperscript{88} quantified the relationship between polystyryl lithium and toluene at 60°C. A relationship between the number average
degree of polymerisation and the chain transfer constant was derived as follows:

\[ x_n = \frac{[M]X}{[SLi]} - C_{RH}[RH] \ln(1-X) \]  

(2.11)

where \([M]\) is the monomer concentration, \(X\) is the degree of conversion, \([SLi]\) the chain-end concentration, \([RH]\) the toluene concentration, and \(C_{RH}\) the transfer constant. A value of \(C_{RH}\) was found to be \(5 \times 10^{-6}\). If polymerisations are carried out rapidly (i.e. in minutes) and the living polymer terminated quickly, the effect of chain transfer can be ignored.

It has been widely reported that spontaneous termination of living polymers can occur. Living polymers are not immortal as they do not have an infinite lifetime and the term should be used with care. The loss of hydride ion from a C-H bond adjacent to a carbanion leads to the formation of a metal hydride and a double bond. If the living polymer solution is stored for any length of time, this slow destruction of the growing ends occurs.

Spach et al. reported a change in the absorption spectra of living polystyrene when left at room temperature for a few days. The peak maxima at 340nm gradually diminishes and a new peak at 535nm appears. The isobestic point shows constant stoichiometry (i.e. no termination by impurities). The solvent used was benzene but similar results were obtained for THF, dioxane.

\(\alpha\)-Methylstyrene also showed a similar mechanism. Although the above work has involved sodium as a counterion, similar reactions can be envisaged involving lithium. Some evidence exists which suggests that the stability of the styryl active centres in ethers is counterion dependent and changes in the order of Li>Na>K.

It is well known that alkyl lithiums react directly with ethers via proton abstraction or ether cleavage. Many anionic polymerisations are studied in ethereal solvents e.g. THF. The growing carbanions may react with the ethers, to form
alcoholates. Fetters\textsuperscript{94} concluded that this process could be arrested by low temperature.

2.5.1.2 Anionically Polymerised Macromonomers

There are two types of macromonomer prepared by anionic polymerisation techniques. The first involves the use of an unsaturated initiator. The second terminates the living polymer with an unsaturated electrophile.

(i) Use of polymerisable initiator.

Of the two methods described above, this has the disadvantage that the unsaturation is generally sensitive to attack by carbanions. However, 4-vinylbenzyl lithium has been shown to be effective in the polymerisation of styrene to produce monofunctional macromonomers\textsuperscript{95}. Also, polymerisations involving oxanionic sites are preferable, since alkoxides do not generally attack carbon-carbon double bonds. Saegusa\textsuperscript{96}, has described a method of producing poly(ethylene oxide) macromonomers containing a heterocycle at the chain end, which can subsequently undergo cationic ring-opening polymerisation.

(ii) Use of a polymerisable deactivator.

End capping of living polymeric anions is the most favoured method for making macromonomers. The major concern is that deactivation occurs without any side reactions. Deactivation of carbanions by means of electrophiles (Wurtz type reactions) is not always fast and quantitative. Undesirable side reactions are quite common and therefore proper characterisation of the macromonomers is essential.

Benzyl halides are well known as efficient deactivators for living polystyrene, but side reactions do occur. The reaction of a styryl carbanion with p-vinyl benzylchloride competes with a side reaction involving attack of the double bond of p-vinyl benzylchloride.

Asami\textsuperscript{14} studied this reaction, the reaction was found to be strongly influenced by the nature of the solvent. Asami
concluded that when the reaction medium contains tetrahydrofuran (THF) no side reaction was observed. Alternatively, the nucleophilicity of the carbanion can be reduced using 1,1-diphenylethylene\textsuperscript{97,98,99}; this then prevents the side reaction. It has been shown recently, that ethylene oxide cannot be used because the alkoxide formed does not react with vinyl benzyl chloride\textsuperscript{100}. A wide range of electrophiles can be used to produce polymerisable end-groups, as shown in table 2.1.

The major advantage of anionic methods is the 'living' nature of the polymers, when transfer and termination reactions are negligible\textsuperscript{74}. The functional purities of macromonomers prepared by anionic polymerisation is high (>90%). However, there are a number of disadvantages. The number of monomers which can be polymerised anionically is limited. Low temperatures may be required and a high vacuum or an inert gas blanket is necessary with ultra-pure reagents and solvents to prevent side reactions.

2.5.2 Cationic methods

(i) Heterocyclic monomers.

Cationic ring-opening polymerisation of some heterocycles such as THF, with some initiators proceed by termination free reaction and without transfer to monomer\textsuperscript{113,114}, i.e. they are living systems. Unsaturated cationic initiators can be used if its double bond cannot take part in polymerisation and if initiation proceeds exclusively by addition. Alternatively, a living polymer chain can be deactivated by reacting an active site with an unsaturated nucleophile, so long as side reactions do not take place. Poly(tetrahydrofuran) macromonomers have been prepared with methacrylate\textsuperscript{115}, acrylate\textsuperscript{116}, p-vinylphenoxyl\textsuperscript{117} and p-vinylbenzyloxy\textsuperscript{118} polymerisable end-groups.

(ii) Vinyl monomers.
<table>
<thead>
<tr>
<th>Initiator</th>
<th>Monomer</th>
<th>Deactivator</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>sec-butyl lithium</td>
<td>styrene</td>
<td>ethylene oxide/methacryloyl chloride</td>
<td>101,102</td>
</tr>
<tr>
<td>n-butyl lithium</td>
<td>styrene</td>
<td>allyl chloride</td>
<td>101</td>
</tr>
<tr>
<td>n-butyl lithium</td>
<td>styrene</td>
<td>diphenylethylene/p-bromomethylstyrene</td>
<td>14,102,103</td>
</tr>
<tr>
<td>n-butyl lithium</td>
<td>styrene</td>
<td>diphenylethylene/vinylidimethylchlorosilane</td>
<td>104</td>
</tr>
<tr>
<td>n-butyl lithium</td>
<td>2-vinylpyridine</td>
<td>p-bromomethylstyrene</td>
<td>105,106</td>
</tr>
<tr>
<td>n-butyl lithium</td>
<td>4-vinylpyridine</td>
<td>methacryloyl chloride</td>
<td>107</td>
</tr>
<tr>
<td>potassium ethoxide</td>
<td>ethylene oxide</td>
<td>p-vinylbenzylchloride</td>
<td>107,108</td>
</tr>
<tr>
<td>triphenylmethyl sodium</td>
<td>t-butyl methacrylate</td>
<td>p-vinylbenzylchloride</td>
<td>109</td>
</tr>
<tr>
<td>triphenylmethyl sodium</td>
<td>methyl methacrylate</td>
<td>p-vinylbenzylchloride</td>
<td>107,110</td>
</tr>
<tr>
<td>n-butyl lithium</td>
<td>hexamethylycyclotrisiloxane</td>
<td>chorosilane</td>
<td>111,112</td>
</tr>
</tbody>
</table>
Vinyllic monomers such as isobutene, styrene and vinyl ethers are generally impeded by several transfer processes. Kennedy\textsuperscript{119} developed a method for producing macromonomers by the so called "inifer" method, which kinetically favours transfer to the initiating species with respect to other transfer reactions (see figure 2.14).

Polyisobutene macromonomers bearing a styryl end group have been synthesised by Kennedy\textsuperscript{119}. The initiating species is p-vinyl benzyl chloride, triethylaluminium and water. A side reaction involving the styryl end group can be envisaged.

### 2.5.3 Free-radical Polymerisation

Macromonomers can be obtained by free-radical polymerisation using matched chain transfer agents and a functional initiator\textsuperscript{120}. Termination must be by chain transfer to this agent, this must then be able to initiate a new chain with a rate constant similar to that of propagation (see figure 2.15).

Table 2.2 shows some of the macromonomers synthesised by this method. Free radical polymerisations have some drawbacks such as broad molar mass distributions and mean functionality. However, it can be applied to a far greater range of monomers compared to anionic methods and does not require the same degree of experimental control.

### 2.5.4 Group-transfer Polymerisation

Group transfer polymerisations are considered to be living and therefore can be used to obtain macromonomers. Webster et al\textsuperscript{121} first introduced terminal functional groups onto PMMA using figure 2.16(a).

Asami et al\textsuperscript{122}, synthesised PMMA macromonomers by two more direct techniques, the first only produced 83% functionality, while the second 100% (see figure 2.16(b)).

### 2.5.5 Polyaddition Processes

The most noteworthy example of polyaddition type synthesis is of polyamine macromonomers prepared by Tsuruta\textsuperscript{130}. Lithium
**FIGURE 2.14**

**THE SYNTHESIS OF MACROMONOMERS BY THE 'INIFER' TECHNIQUE**

$$RCl_3 + BCl_3 \equiv [R^\oplus BCl_4^\ominus]$$  
*Complex formation*

$$[R^\oplus BCl_4^\ominus] + CH_2=CH_2 \rightarrow R-CH_2-CH_2 BCl_4^\ominus$$  
*Initiation*

$$\sim CH_2-CH_2 BCl_4^\ominus + CH_2=CH_2 \rightarrow \sim \sim CH_2-CH_2 BCl_4^\ominus$$  
*Propagation*

$$\sim \sim CH_2-CH_2 BCl_4^\ominus \rightarrow \sim \sim CH_2-CH_2 BCl_4^\ominus + BCl_3$$  
*Anion Splitting*

$$\sim \sim CH_2-CH_2 BCl_4^\ominus + RCl \rightarrow \sim \sim CH_2-CH_2 BCl_4^\ominus + [R^\oplus BCl_4^\ominus]$$  
*Transfer to RCl*

where $RCl_3$ = initiator and chain transfer agent  
$BCl_3$ = coinitiator
FIGURE 2.15
FUNCTIONALISATION USING A MATCHED FREE-RADICAL INITIATOR AND CHAIN TRANSFER AGENT

INITIATOR: \( \text{CH}_3 - C - N = N - C - \text{CH}_3 \) \[ \Delta \] 2 \( \text{CH}_3 - C^\bullet \) + \( N_2 \)

DECOMPOSITION:

INITIATION: \( \text{CH}_3 - C^\bullet \) + \( M \) \rightarrow \( \text{CH}_3 - C - M^\bullet \)

PROPAGATION: \( \text{CH}_3 - C - (M)_n - M^\bullet \)

CHAIN TRANSFER:

\( \text{CH}_3 - C - (M)_n - M^\bullet \) + \( \text{HSCH}_2\text{COOH} \) \rightarrow \( \text{CH}_3 - C - (M)_n - MH \)

\( \text{SCH}_2\text{COOH} \) + \( nM \) \rightarrow \( \text{HOOCCH}_2\text{S}-(M)_{n-1} - M^\bullet \)
<table>
<thead>
<tr>
<th>Monomer</th>
<th>Chain Transfer Reagent</th>
<th>Capping Agent</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>MMA</td>
<td>thioglycollic acid</td>
<td>glycidyl methacrylate</td>
<td>123,124</td>
</tr>
<tr>
<td>stearyl methacrylate</td>
<td>thioglycollic acid</td>
<td>glycidyl methacrylate</td>
<td>125</td>
</tr>
<tr>
<td>methacrylic acid</td>
<td>thioglycollic acid</td>
<td>glycidyl methacrylate</td>
<td>126,127</td>
</tr>
<tr>
<td>ethyl methacrylate</td>
<td>thioglycollic acid</td>
<td>glycidyl methacrylate</td>
<td>126,127</td>
</tr>
<tr>
<td>butyl methacrylate</td>
<td>thioglycollic acid</td>
<td>glycidyl methacrylate</td>
<td>126,127</td>
</tr>
<tr>
<td>lauryl methacrylate</td>
<td>thioglycollic acid</td>
<td>glycidyl methacrylate</td>
<td>126,127</td>
</tr>
<tr>
<td>vinyl pyrrolidone</td>
<td>mercaptopropionic acid</td>
<td>chloromethylstyrene + phase transfer catalyst</td>
<td>128</td>
</tr>
<tr>
<td>dodecyl acrylate</td>
<td>mercaptoethanol</td>
<td>acryloyl chloride</td>
<td>129</td>
</tr>
</tbody>
</table>
FIGURE 2.16
THE SYNTHESIS OF MACROMONOMERS BY GROUP TRANSFER POLYMERISATION

\[
\begin{align*}
\text{CH}_2=\text{CH} & + n \text{ CH}_2=\text{C} \quad \xrightarrow{(i) HF^+} \quad \text{CH}_2=\text{CH} \\
\text{Me} & \quad \text{CO}_2\text{Me} \\
\text{OSiMe}_3 & \\
\end{align*}
\]

\[
\begin{align*}
\text{(Me)}_2\text{C} & \quad \xrightarrow{\text{MeOH}} \quad \text{CH}_2=\text{CH} \\
\text{CO}_2\text{Me} & \quad \text{CO}_2\text{Me} \\
\text{OSiMe}_3 & \quad \text{n-1} \\
\end{align*}
\]

\[
\begin{align*}
\text{BrCH}_2 & \quad \xrightarrow{} \quad \text{CH}=\text{CH}_2 \\
\text{Me} & \quad \text{OMe} \\
\text{OSiMe}_3 & \\
\end{align*}
\]

\[
\begin{align*}
\text{(Me)}_2\text{C} & \quad \xrightarrow{} \quad \text{CH}_2=\text{C} \\
\text{CO}_2\text{Me} & \quad \text{CO}_2\text{Me} \\
\text{n} & \\
\end{align*}
\]
diisopropylamide catalyses the reactions of N,N-diethylethylenediamine and piperazine with 1,4-divinylbenzene (see figure 2.17).

2.6 COPOLYMERISATION THEORY OF CONVENTIONAL MONOMERS

Copolymerisation involves the simultaneous polymerisation of two or more monomers to form products which contain two or more different structures in the chain. All major polymerisation techniques (free-radical, ionic, and coordination) may be used to give four basic types of copolymer structure: statistical, alternating, block and graft.

2.6.1 The Terminal Model and Reactivity Ratios

Copolymer composition and microstructure depend upon the relative concentrations of the comonomers and their reactivities toward each other. The Terminal model assumes that the rate of monomer addition to a growing chain end depends only on the nature of the end group of the chain. The copolymer composition equation can be derived131,132.

\[
\frac{d[M_1]}{d[M_2]} = \frac{[M_1] (r_1[M_1] + [M_2])}{[M_2] ([M_1] + r_2[M_2])} \tag{2.12}
\]

The terminal model assumes that the copolymer chains have high molar masses and that the monomer is only consumed by propagation reactions. The monomer reactivity ratios, \(r_1\) and \(r_2\), are the ratios of the rate constant for a given reactive species adding its own monomer to the rate constant for its adding the other monomer. The tendency of the two monomers to copolymerise is defined by their \(r\) values. Thus \(r_1 > 1\) means that the reactive species adds \(M_1\) preferentially, with \(r_1 < 1\), \(M_2\) is preferred.
FIGURE 2.17
THE SYNTHESIS OF MACROMONOMERS BY POLYADDITION PROCESSES

C₂H₅NHCH₂CH₂NH₂H₅ + CH₂=CH—CH=CH₂

\[ \text{LiN}_R \]

CH₂=CH—CH₂—CH₂—N—CH₂CH₂—NH—C₂H₅

\[ \text{C₂H₅} \]

Self-Polyaddition \[ \text{etc LiN}_R \]

MACROMONOMER
2.6.2 Types of Copolymerisation

If \( r_1 \) \( r_2 \) is unity an ideal system is said to exist. Therefore, the reactivities of both propagating chains are the same.

\[
\frac{k_{22}}{k_{21}} = \frac{k_{12}}{k_{11}} \quad \frac{d[M_1]}{d[M_2]} = r_1 \frac{[M_1]}{[M_2]} \tag{2.13}
\]

The relative rate of incorporation of the two monomers is independent of the unit at the end of the propagating chain.

If \( r_1 = r_2 = 0 \), the radicals react exclusively with the other monomer. The monomers alternate regularly along the chain.

Most systems lie between the ideal and alternating cases. For cases when \( r_1 \) and \( r_2 \) are less than unity, there is a certain feed composition which produces an identical copolymer composition. This is known as an azeotropic polymerisation and proceeds without a change in composition of the feed or copolymer.

\[
\frac{[M_1]}{[M_2]} = \frac{(1-r_2)}{(1-r_1)} \tag{2.14}
\]

Block Copolymerisation occurs when both \( r_1 \) and \( r_2 \) are greater than one. Each propagating species prefers to react with its own monomer tending to form a blocky copolymer, in which there are blocks of both monomers in the chain.

2.6.3 Copolymer Composition and Conversion

The copolymerisation equation gives only the instantaneous copolymer composition formed at low degrees of conversion (less than 5%). Therefore, the comonomer feed will change in composition as one of the monomers adds preferentially into the copolymer (except for azeotropic copolymerisations) with
increasing conversion. A drift will be observed to a composition rich in the less reactive monomer.

Attaining a copolymer with a narrow composition distribution is desirable, since copolymer properties often depend on composition. The heterogeneity in the copolymer composition can be minimised by:

(1) Restricting the degree of conversion

(2) Choosing two monomers whose copolymerisation behaviour results in copolymer compositions similar to the feed.

(3) The batchwise or continuous addition of the more reactive monomer, thereby maintaining the feed approximately constant.

Stockmayer\textsuperscript{134} showed that the spread in copolymer composition due to statistical fluctuations was small in practical cases. For alternating copolymers the spread in composition was minimal; even for ideal copolymers, where the spread is greater and is a function of the degree of polymerisation the effect is not large, and follows a gaussian distribution. It is possible to calculate the probability of the occurrence of sequences of \( n \) similar monomer units for an ideal copolymer\textsuperscript{135}. The number \( N(n) \) of such sequences is

\[
N(n) = p^{n-1}(1-p)
\]  

(2.15)

where \( p \) is the probability of addition of that monomer,

\[
p = \frac{r_1[M_1]}{r_1[M_1]+[M_2]}
\]

(2.16)

Except for a monomer present in large excess (such as graft copolymerisation), the sequences are always short. Obviously, the larger the molar mass of the copolymer the lower the probability of homopolymer formation.
2.6.4 Experimental Determination of Reactivity Ratios

For many systems, it is assumed that the terminal model is valid. If copolymerisations have been performed at low conversions, then the instantaneous copolymerisation equation applies. If on the other hand, polymerisations have been carried to high conversion then an integrated form of this equation is required, since the final feed ratio will be different to the initial ratio. Reactivity ratios are most often determined over a wide range and number of feed compositions. It is possible to measure copolymer compositions either directly or by measuring the concentration of unreacted monomers.

(i) Fineman-Ross Method\textsuperscript{136}

This technique and the Kelen-Tudos method involve converting the instantaneous copolymerisation equation into a linear form for the parameters $r_1$ and $r_2$ and then estimating the reactivity ratios by linear least squares.

If $F$=feed composition and $f$=copolymer composition then :-

$$F(f-1) = \frac{r_1F^2}{f} - \frac{r_2}{f} \quad (2.17)$$

Therefore, a plot of $F(f-1)/f$ versus $F^2/f$ gives a slope of $r_1$ and an intercept of $r_2$.

(ii) Kelen-Tudos Method\textsuperscript{137}

The disadvantage of Fineman-Ross is the excessive weighting of extreme data points. This can be avoid by spreading the data on the axes. By defining $G = F(f-1)/f$ and $H = F^2/f$, the following linear equation applies.
Therefore, by plotting $G/(\alpha+H)$ versus $H/(\alpha+H)$, $r_1$ and $r_2$ can be calculated from linear least squares analysis.

There are other alternative methods of determining reactivity ratios using non-linear regression techniques\(^{138}\). These are however not so widely used as the above methods. When there is a drift in feed and copolymer composition with conversion, the copolymer composition at any one time is an average of all the polymer made up to that point. If the monomer composition is being analysed, an integrated form of the copolymer composition equation can be used. The error in variables method (EVM) can be used for composition data over a range of conversions\(^{139,140}\). Instead of assuming that errors only occur in the dependant variable (i.e. the copolymer composition), all sources of experimental error are accounted for.

2.6.5 Alternative Copolymerisation Models

In certain situations, the terminal model for copolymerisation does not hold. A number of alternative models have been proposed. Alfrey and Goldfinger\(^{141}\) proposed that the penultimate group also had an influence on the copolymerisation reactivity of the propagating radical. The penultimate effect has been observed in free radical copolymerisations where the monomers contain highly bulky or polar substituents i.e. styrene and acrylonitrile.

If one of the comonomers contain electron-donating substituents and the other electron-withdrawing groups, the copolymerisation shows a tendency to produce alternating copolymers. It is thought that a 1:1 donor-acceptor complex participates in propagation. This is called complex-participation, complex dissociation can also occur but the
complexes do not add in a concerted fashion with only one of the complexed monomers being added to the propagating chain.

All the models discussed so far assume that copolymerisations are irreversible. If however, the ceiling temperature is approached, the influence of depropagation must be considered. Lowry\textsuperscript{142} has developed a theory based on the copolymerisation equation if one of the two monomers is reversible.

It is not possible to determine from the composition data alone which model is correct. Comonomer sequence distributions must be analysed to discriminate between the models. Comonomer sequence distributions are sensitive to the details of the chain growth process. $^{13}$C Nuclear Magnetic Resonance spectroscopy is one method used to analyse copolymer sequences. It is also possible to calculate comonomer sequence distributions for the various models knowing the reactivity ratios and the comonomer feed ratios, or using the Monte Carlo Approach. By comparing experimental data with the predicted models, it is possible to identify the correct model for the copolymerisation under study.

2.6.6 Radical and Monomer Reactivities in Copolymerisation

The reaction between a radical and a monomer depends on their reactivities. These reactivities depend on the nature of the substituents which can influence reactivity through resonance, steric and polar effects.

(i) Resonance Effects

The reactivity of monomers depends on the resonance stabilisation of the radical produced from the monomer. Delocalisation of $\pi$-electrons improves the resonance stabilisation. The order of substituents in enhancing radical reactivity is opposite to that for monomer reactivity. A substituent which increases monomer reactivity does so because it stabilises and decreases the reactivity of the corresponding radicals.
(ii) Steric Effects

Steric hindrance effects the rate of radical-monomer reaction. This is clearly seen in chlorinated vinyl monomers, e.g. vinyl chloride>vinylidene chloride>1,2-dichloroethylene

(iii) Polar Effects

Monomers will tend to alternate as the difference in polarity between two monomers increases. Monomers with electron donating and electron withdrawing substituents have widely differing polarities and, when copolymerised with each other, can produce highly alternating copolymers. It is thought that this results from the homopolymerisation of 1:1 complexes formed. The addition of a Lewis acid, such as trialkyl aluminium, can increase the tendency to form alternating polymers.

(iv) Solvent Effects

Free-radical copolymerisations are generally carried out in solution. Copolymerisations involving non-polar monomers with monomers containing ionisable groups, groups capable of hydrogen-bonding interactions or even polar groups may show a marked influence depending on the nature of the solvent. This will give rise to changes in measured reactivity ratios, varying with solvent. Harwood has found that, although the reactivity ratios may vary considerably as the reaction solvent is changed, the copolymers with identical compositions had the same microstructure. Harwood proposed that the partitioning of monomers between solvent and growing radicals was important. The reactivity ratios determined for polar monomers were products of the true reactivity ratios and the partition coefficients. The reactivity ratios are therefore independent of solvent but the solvent will influence the relative local concentrations of the comonomers to the growing chain end.
2.7 THE COPOLYMERISATION OF MACROMONOMERS WITH COMONOMERS

2.7.1 General Features

The free radical copolymerisation of macromonomers with monomers to yield graft copolymers is their major application. The ability of macromonomers to polymerise differs from conventional monomers due to the following reasons\(^\text{10,102,146}\).

(i) The molar concentration of macromonomer is lower because of its molar mass \((M_n=5\times10^2\) to \(2\times10^4\)).

(ii) The reactivity of the terminal double bond may be reduced compared to similar low molar mass monomers, due to the influence of the bulky chain.

(iii) If the chain segments of the macromonomer can give rise to transfer reactions, the probability is increased because of the number of repeat units present.

To date, a large number of papers have been written dealing with the free radical copolymerisation of macromonomers. Generally copolymerisations have been carried out in solution and the molar masses of the graft copolymers produced are generally low \((M_n<80,000)\)^\text{111,147}. A number of reasons have been offered for this low molar mass including:

(a) Low concentration of double bonds\(^\text{111,146,147,148}\).

(b) The low mobility of the macromonomer and lack of access of the reactive site\(^\text{147}\).

(c) Transfer reactions\(^\text{147,148}\).

It can be concluded that the lifetime of a radical is too short to allow sufficient number of growth steps necessary for high molar masses to occur. Homopolymerisation of macromonomers has in general been found to be difficult. In general, for solution homopolymerisation, the degrees of polymerisation are very low and/or degrees of conversion are low\(^\text{102,147,148}\). In some cases, no polymerisation has been observed at all\(^\text{149}\). Kennedy and Hiza\(^\text{149}\) observed that when poly(isobutenyl...
methacrylate) macromonomers were homopolymerised, the molar mass did not increase, but the vinyl group concentration in the macromonomer decreases. Bulk polymerisation of poly(isobutenyl methacrylate) macromonomers was possible\textsuperscript{105,149}. This is thought to be due to the Trommsdorf effect, with the entrapment of radicals thus preventing termination. Recently a more thorough study has been carried out of the homopolymerisation behaviour of macromonomers\textsuperscript{150}. It was found that the degree of polymerisation was strongly dependant on concentration as a result of a pronounced gel effect. If the macromonomer concentration is too low, the rates of propagation and termination are suppressed by (a) or (b) above, whereas the rate of chain transfer will remain unaffected. When the macromonomer concentration is increased, the viscosity is also increased. Therefore, increasing the rate of propagation and reducing termination, resulting in higher molar masses.

2.7.2 Copolymer Composition in Macromonomer Copolymerisations

If the terminal model is valid, the reactivity ratios of macromonomers determines their ability to participate in copolymerisation. In graft copolymerisation there is a large difference in the molar concentrations of the macromonomer and comonomer in the feed. Under such circumstances, the copolymerisation equation can be simplified as proposed by Jaack's\textsuperscript{151}. The following assumption holds true.

\[
[M] \ll r_A[A] \text{ and } r_m[M] \ll [A] \quad (2.19)
\]

\(M = \text{macromonomer and } A = \text{comonomer}\)

As a result the copolymerisation equation reduces to

\[
\frac{d[A]}{d[M]} = \frac{r_A[A]}{[B]} \quad (2.20)
\]
This implies that the value of \( r_2 \) is insignificant to the process, provided the molar concentration of macromonomer in the feed is small. Chain propagation is assumed to take place almost exclusively by addition to polymer radicals with a terminal \( M_1 \) unit. This provides a method for determining \( r_1 \) in macromonomer copolymerisations.

2.7.3 Graft Copolymer Composition Distribution

Attaining a copolymer with a narrow composition distribution is desirable, since copolymer properties often depend on composition.

(i) Statistical Chemical Heterogeneity

Stejskal et al\(^{152,153,154}\), have predicted that the chemical composition distribution (CCD) for graft copolymers prepared by the copolymerisation of macromonomers is much broader than for conventional copolymers, and becomes wider and more asymmetrical with higher molar mass macromonomers. However, the graft copolymer CCD decreases as the degree of grafting increases. The chemical heterogeneity will also decrease when the backbone molar mass increases.

(ii) Conversion Chemical Heterogeneity

The copolymerisation equation gives only the instantaneous composition formed at low degrees of conversion. As the degree of conversion increases, there is a drift in the comonomer (and hence copolymer) composition towards the less reactive monomer, resulting in conversion chemical heterogeneity. In the case of graft copolymerisation, there is a very low molar concentration of macromonomer. Therefore, the drift in feed ratio is not so marked as in the simple random copolymerisation of two low molar mass comonomers\(^{155}\). Conversion chemical heterogeneity in the copolymer composition can be minimised by:

(1) restricting the degree of conversion;

(2) choosing two comonomers whose copolymerisation behaviour results in copolymer compositions similar to the feed;
(3) the batchwise or continuous addition of the more reactive monomer, thereby maintaining the feed approximately constant.

2.7.4 Macromonomer Reactivity in Copolymerisation

Much interest has been focused on whether the functional group in a macromonomer has the same reactivity as the low molar mass analogue. At the present time, the copolymerisation behaviour of macromonomers is uncertain. It is unclear whether the polymer chain affects the reactivity of the terminal functional group. It is difficult to determine the reactivity ratio of the macromonomer ($r_2$) because of its low molar concentration. Values for the comonomer reactivity ratio ($r_1$) have been reported extensively and most of the information is gained from such determinations.

(i) Macromonomer End-group

Some of the literature suggests that the reactivity of macromonomers does not differ from their low molar mass analogues. In these cases, the reactivity is assumed to be governed only by the functional end group and is independent of molar mass. Therefore, the macromonomer reactivity is governed only by resonance, steric and polar effects associated with the end-group.

(ii) Macromonomer Chain Length

There have been a number of reports that macromonomer reactivity is lower than their respective low molar mass monomers. Three factors are have been reported to contribute to this effect.

(a) Kinetic excluded volume effect.

This is a type of diffusion controlled reaction, as a result of the size of the macromonomer chain and the rate at which the reactive end group can be attacked by the propagating radical. As a consequence of diffusion control, reactivity decreases with increasing molar mass.11,108,116,163,164.
(b) Incompatibility between unlike polymers.

The thermodynamic repulsive interaction between macromonomer and a propagating comonomer chain results in a heterogeneous distribution of the polymerisable end group in the reaction system. As a consequence of this;

(i) macromonomer reactivity will decrease with increasing molar mass\textsuperscript{108,128,165}.

(ii) conversion will decrease with increasing macromonomer molar mass\textsuperscript{128}

(iii) macromonomer reactivity decreases with conversion\textsuperscript{11}

(iv) incomplete macromonomer conversion is observed due to phase separation\textsuperscript{101}

In such systems, it is likely that the factors determining polymer-polymer-solvent compatibility will influence macromonomer reactivity. These are the relative amounts of the two polymer chains, the interaction parameter between the two chains (this is molar mass dependent) and the nature of the solvent.

(c) Effect of solvent.

Thermodynamic repulsive interactions may arise between a macromonomer and the propagating comonomer chain, due to the solvent\textsuperscript{165,166,167}. The degree of penetration may be affected because of the different expansion or swelling of the polymer coils. The volume fraction of the solvent is another important factor, as a mixture of two polymers in a common solvent has a limited compatibility.

Therefore, any parameter affecting the mobility of the macromonomer chains will also affect the polymerisation. The rate of polymerisation is decreased with increasing molar mass of the macromonomer. The conversion will decrease as the macromonomer molar mass or feed concentration is increased. The reactivity will also decrease with increasing conversion and
macromonomer content will decrease with higher catalyst concentration because of their lower mobility at higher yields.

Tsukahara et al.\textsuperscript{167} demonstrated the solvent can effect macromonomer reactivity. Copolymerisation of a methacrylate terminated poly(dimethylsiloxane) macromonomer with methyl methacrylate was carried out in benzene (a good solvent) and phenetol (a poor solvent for the macromonomer). For low molar mass macromonomers they found the reactivity ratios were identical for conventional copolymerisations. However, for high molar mass macromonomers they observed the same reactivity in benzene, but markedly reduced in phenetol. The solvent can affect the reactivities of the monomers rather than the macromonomer chain length, in a similar manner to conventional copolymerisations.

2.8 \textbf{SMALL-ANGLE X-RAY SCATTERING (SAXS)}

Small-angle X-ray scattering provides a method for determining particles dispersed in a matrix with dimensions from ca. 10\textgreek{A} up to 1000\textgreek{A}. It can be used for analysing crystal lamellae in semi-crystalline polymers, incompatible polymer blends and micelles in solution. In dense systems, the periodicity between two phases is observed, whilst in dilute systems the dimensions of one of the phases is observed.

The ideal mathematical geometry for SAXS is a pinhole collimated camera. However, the scattered intensity obtained is not sufficient for practical applications. Therefore, slit collimation is used to increase beam intensity. A slit can be considered to be equivalent to a large number of pinholes stacked on each other. The resultant scattering pattern is an interference pattern constructed from all of the pinhole patterns. The scattering data must therefore be manipulated to approximate to pinhole optics. This means 'desmearing' of the scattered intensities. Alternatively, the mathematical relationships can be smeared to circumvent this approximation.
2.8.1 Determination of Particle Size

Guinier\textsuperscript{168,169} proposed that for a dilute, monodisperse system in which particles assume all orientations with equal probability, the scattered intensity can be described by

\[ I(\theta) = I(0) \exp\left(-\left(\frac{4\pi\theta}{\lambda}\right)^2 R_g^2\right)/3 \] (2.21)

\[ \ln I(\theta) = \ln I(0) - \left(\frac{4\pi\theta}{\lambda}\right)^2 R_g^2/3 \] (2.22)

where \( I(\theta) \) and \( I(0) \) are the desmeared intensities at \( \theta \) and zero angle respectively; \( R_g \) is the radius of gyration and \( s \) is the angular variable \( (s=(2\sin(\theta)/\lambda)) \). A plot of \( \ln I(\theta) \) against \( 4\pi s^2/3 \) enables the radius of gyration to be determined from \(-\)gradient\( )^{0.5} \). For spherical particles the radius of a particle \( (R_{sp}) \) is given by

\[ R_{sp} = (5/3)^{\frac{1}{2}} R_g \] (2.23)

2.8.2 Determination of Fringe Thickness

Porod\textsuperscript{170,171,172} showed that for a sharp interfacial boundary for an ideal two-phase system a decrease in smeared intensity proportional to the reciprocal third power of \( s \). Polymers often show systematic deviations from Porod's law i.e. A plot of \( I_s^3 \) vs \( s \) does not reach a constant value. This deviation if negative may be interpreted in terms of a diffuse interfacial layer between the two phases.

Two models have been employed to describe the change in electron density between the particle core and the diluent. Vonk\textsuperscript{173} used a linear model and Ruland\textsuperscript{174} a sigmoidal-gradient model (see figure 2.18). The graphical solutions to these models have a limited range of applicability depending on the approximations used\textsuperscript{175}. The graphical solutions have also been smeared to allow the use of smeared scattering intensities. Table 2.3 lists the range of applicability for each of the solutions.
FIGURE 2.18
ELECTRON DENSITY PROFILE $p_{\text{obs}}(r)$ AND SMOOTHING FUNCTION $h(r)$
FOR (a) SIGMOIDAL MODEL AND (b) LINEAR GRADIENT MODEL

A

Electron density profile

B

Electron density profile

Smoothing function

$\sigma$

$\delta$

$h(r)$
TABLE 2.3
RANGE OF APPLICABILITY FOR SMEARED POROD RELATIONS
(WITH INFINITE SLIT ASSUMPTION)

<table>
<thead>
<tr>
<th>Applicability Approximation</th>
</tr>
</thead>
</table>

**Linear Gradient Model**

Vonk

$$I(s) = (k'/s^3)(1-2s^2\delta^2s^2/3)$$

$$\delta s < 0.10$$

**Sigmoidal Gradient Model**

Empirical

$$I(s) = (k'/s^3)\exp(-38(\delta s)^{1.81})$$

$$0.009 < \delta s < 0.72$$

$$k' = w_i(0)k_p\delta/2$$

$$s = 2.\sin\theta/\lambda$$

$$\delta = 120.5.\delta$$

$$\delta = \text{interfacial layer thickness}$$
3 EXPERIMENTAL

3.1 CHEMICALS USED

2,2 Azobis(isobutyronitrile) (AIBN) supplied by Fluka Chemie AG was recrystallised from methanol.

Benzophenone, SLR grade was used as supplied by Aldrich Chemical Co Ltd.

Bis-hydroxyethyl terephthalate (BHET), was used as supplied by ICI Wilton Materials Research Centre.

Calcium Hydride, 95+% (CaH₂) was used as supplied by Aldrich Chemical Co Ltd as a coarse ground powder.

Chloroform (CHCl₃), SLR grade was used as supplied by Carless Solvents.

Cyclohexane SLR grade was used as supplied by Carless Solvents.

Di-butyl Magnesium (1.0M) in heptane, was used as supplied by Aldrich Chemical Co Ltd.

Dichloromethane, SLR grade was used as supplied by Carless Solvents.

Diethyl Ether, SLR grade was used as supplied by Carless Solvents.

Dimethylformamide (DMF), SLR grade was used as supplied by Fisons PLC for polymerisations.

Dimethylformamide (DMF), HPLC grade was used with 0.1% by wt LiBr for GPC, supplied by Fisons PLC.

1,1-diphenyl ethylene, 99% was dried over Calcium hydride prior to use, supplied by Aldrich Chemical Co Ltd.

Fluorene, SLR grade was used as supplied by Aldrich Chemical Co Ltd.

Hydrochloric Acid (HCl), specific gravity 1.38 SLR grade supplied by Fisons PLC, diluted with deionised water to correct molarity.
Lithium Bromide (LiBr), AR grade was used as supplied by Fisons PLC.

Manganese II acetate tetrahydrate was used as received from ICI Wilton Materials Research Centre.

Methanol, SLR grade was distilled prior to use for dispersion experiments, and was supplied by Carless Solvents.

Methylcyclohexane, SLR grade, was dried over calcium hydride prior to use, supplied by Aldrich Chemical Co Ltd.

Methyl methacrylate, 99% pure inhibited with 10ppm hydroquinone monomethyl ether was vacuum distilled prior to use, supplied by Aldrich Chemical Co Ltd.

Petroleum Ether 40-60, SLR grade was used as supplied by Carless Solvents.

Potassium Hydroxide Pellets, SLR grade was used as supplied by Fisons PLC.

Pyrrolidone, 99% pure was dried over CaH₂ before use and was supplied by Aldrich Chemical Co Ltd.

Sec-butyl lithium (1.3M) in hexane, was used as supplied by Aldrich Chemical Co Ltd.

Sodium, 99% was rinsed in petroleum ether prior to use, supplied by Aldrich Chemical Co Ltd.

Styrene, 99% pure inhibited with 10-15 ppm 4-tert-butylcatechol supplied by Aldrich Chemical Co Ltd. This was purified by vacuum distillation before use.

Triethylamine, 98% pure SLR grade, was dried over KOH and distilled before use, and was supplied by Fisons PLC.

Tetrahydrofuran, HPLC grade, was used as supplied for GPC and dried over calcium hydride prior to use in polymerisations, supplied by Fisons PLC.

Tetraisobutane 90, was used as received from Bayer.

Toluene, SLR grade, was used as supplied by Carless Solvents.
Vinyl Benzyl Chloride, 97% pure mixture of isomers meta:para 60:40 was used as supplied by Aldrich Chemical Co Ltd.

2-Vinyl Pyridine, 97% was vacuum distilled prior to use and was supplied by Aldrich Chemical Co Ltd.

4-Vinyl Pyridine, 96% was vacuum distilled prior to use and was supplied by Aldrich Chemical Co Ltd.

3.2 THE SYNTHESIS OF STYRYL TERMINATED MACROMONOMERS

All macromonomer samples were prepared using anionic polymerisation techniques. These 'living' polymer systems are susceptible to termination from electrophilic impurities such as water or carbon dioxide, so the polymerisations are performed under conditions of very high purity. Such conditions can be achieved by using either inert gas blankets or by high vacuum techniques. For the present work high vacuum techniques are preferred for purifying the reagents and performing the polymerisations.

The general principles of high vacuum work as described by Morton and Fetters were followed. Purification and reactor preparation were performed on a purpose-built vacuum frame. The pumping system consisted of a rotary oil pump and a mercury diffusion pump which was capable of producing a vacuum better than 0.1 Nm\(^{-2}\). Greaseless PTFE taps and joints were used throughout the main section of the frame. Reactors and reactant ampoules were of all-glass construction with extensive use being made of breakseals (figure 3.1). All glassware was rigorously cleaned using chromic acid, washed several times with distilled water and dried. All glassware was strongly flamed above 500K under constant evacuation to remove adsorbed water molecules.

3.2.1 Purification of Reagents

Styrene (Aldrich, 99%, stabilised with 10-15 ppm 4-t-butylcatechol) was dried over freshly ground calcium hydride. Traces of water were removed by using the vacuum frame. The
FIGURE 3.1
TYPICAL HIGH VACUUM REACTANT AMPOULES

initiator ampoule
rubber septum
breakseal
terminator ampoule
monomer ampoule
styrene was firstly degassed using the freeze/thaw technique before being distilled onto a freshly prepared sodium mirror. Finally the last traces of impurities were removed by distilling onto sodium and fluorene. When the styrene is dry, a characteristic orange complex of sodium fluorenyl is formed over 48 hours; this removes nearly all impurities. The styrene was then distilled directly into a pre-flamed ampoule, degassed and sealed off from the vacuum line. The ampoules were stored at 263K until required.

Methylcyclohexane (Aldrich, SLR grade) was dried over freshly ground calcium hydride. The flask of methylcyclohexane was then attached to the vacuum frame and degassed using the familiar freeze/thaw technique. The solvent was then flash distilled onto a freshly prepared sodium mirror; this has a high surface area and removes final traces of moisture. The methylcyclohexane is redistilled until the sodium mirror is intact. Two such distillations were found to be sufficient. The dry methylcyclohexane was then stored over polystyryl lithium on the vacuum frame and then distilled directly into the reactor when required.

Tetrahydrofuran (THF; Fisons, HPLC grade, uninhibited) was dried over freshly ground calcium hydride before being attached to the vacuum frame. Degassing was carried out using the freeze/thaw procedure before distilling onto sodium and benzophenone. This solvent, when dry, produces the characteristic blue sodium/benzophenone/THF complex. The THF is stored over this complex until required, when it is distilling directly into the reactor.

Di-butyl magnesium (Aldrich) 1M in heptane was used as supplied, being transferred to the reactor using dry nitrogen syringe techniques.

Sec-butyl lithium (Aldrich) supplied as a solution in cyclohexane (1.3 M) was not purified before use. The required volume using dry nitrogen syringe techniques was syringed into
the initiator ampoule (figure 3.1) through a rubber septum, and the injection arm sealed off immediately. The initiator solution was then degassed and sealed off from the vacuum line. Initiator ampoules were stored at 263K until required.

1,1-Diphenyl ethylene (Aldrich) was stored over freshly ground calcium hydride. The required volume was then syringed into a flame dried evacuated flask fitted with a PTFE tap containing some calcium hydride. After attaching to the vacuum line and degassing, the diphenyl ethylene was distilled into a flame dried ampoule (see figure 3.1). After degassing and sealing the ampoule off, this was then stored at 263K until required.

Vinyl benzyl chloride was dried over calcium hydride. The required volume was then syringed into a flame dried flask fitted with a PTFE tap containing some calcium hydride. After attaching to the vacuum line and degassing, the capping agent was distilled into a flame dried ampoule (see figure 3.1). After degassing, THF (20ml) was distilled into the ampoule and then sealed off from the vacuum line and stored at 263K until required.

Methanol (SLR grade) was used as supplied as a terminator.

3.2.2 Polymerisation and Endcapping Procedure

The reactant ampoules were sealed onto an all-glass reactor containing a PTFE magnetic stirring bar and a glass covered iron rod, as shown in figure 3.2. The reactor was attached to the vacuum line, evacuated and flamed out until a pressure of 0.1 m Nm⁻² was reached. The methylcyclohexane (250 ml) and THF (50ml) were distilled directly into the reactor from the reservoirs and then degassed. The reactor was then sealed off from the vacuum frame. The di-butyl magnesium was then syringed into the reactor via the rubber septum. The injection arm was then sealed off immediately. The reactor was then rinsed in the solution of di-butyl magnesium to remove any residual impurities adsorbed onto the glass, this was left for one hour.
FIGURE 3.2
REACTOR FOR ANIONIC POLYMERISATION UNDER HIGH-VACUUM

diphenylethylene
monomer

er septa

PTFE bar

initiator
terminator

breakseal

homopolymer ampoule

tap

A

B
The organometallic was removed by pouring the solution into the side flask (A) and distilling out the solvent. The solvent was then poured back into the side flask and the procedure repeated four or five times. This procedure removes virtually all the di-butyl magnesium and its decomposition products from the main reactor. The solvent is finally distilled out of the side arm and the flask is sealed off. The reactor and its contents can then be truly considered to be free of impurities.

The initiator solution was then added to the solvent by crushing the appropriate breakseal with the glass covered iron rod and the ampoule was rinsed with condensing solvent. The reactor was then placed in a cold water bath and the monomer added to the mixture. The characteristic orange-red colour of the polystyryl carbanions was formed immediately. The reaction was stirred for half an hour to ensure complete monomer conversion. Diphenyl ethylene was added at this stage, a dramatic colour change to cherry-red was observed. The reaction mixture was left for half an hour to ensure complete conversion.

A small sample was collected in ampoule (B) by tilting the reactor. The ampoule was then sealed off; this sample was then used for characterisation of the polystyrene.

The remaining 'living' polystyrene solution was reacted with the capping agent by crushing the appropriate breakseal. An immediate loss of colour was observed, indicating termination had occurred.

Purification of the homopolymer and macromonomer was achieved by precipitating in a five-fold excess of methanol and then separating by filtration. Further purification was carried out by dissolving in chloroform and reprecipitating in methanol another three times. The samples were dried in vacuo overnight at room temperature.

Characterisation of these homopolymers and macromonomers was carried out using GPC and $^1$H nmr.
3.3 SYNTHESIS OF N-(VINYL BENZYL)PYRROLIDONE

N-(vinylbenzyl)pyrrolidone was synthesised by adding diethyl ether (100ml), pyrrolidone (30g, 0.35 moles) to ground KOH pellets (16g, 0.4 moles) in a three necked round bottomed flask containing a magnetic follower. A nitrogen blanket was supplied to the flask and after allowing the components to stir for a few minutes, triethylamine (40g, 0.4 moles) was added via a dropping funnel. Finally vinylbenzyl chloride (40g, 0.26 moles) was added over one hour and the reaction mixture left to stir for 24 hours. The crude mixture was then filtered and washed with diethyl ether. The diethyl ether extract was then washed with water, 4M HCl, 0.5M HCl and water. The organic layer was then dried over MgSO₄ and the solvent removed in vacuo. Unreacted vinylbenzyl chloride was removed using the dry flash silica technique, eluting firstly with petroleum ether 40-60: diethyl ether(1:1) and then with only diethyl ether. The diethyl ether fraction contained pure N-(vinylbenzyl)pyrrolidone (42g, 81%). The monomer was then characterised by IR, ¹H and ¹³C nmr and mass spectrometry.

3.4 SYNTHESIS OF HOMOPOLYMER BACKBONES

N-(Vinyl benzyl)pyrrolidone, 2-vinyl pyridine and 4-vinyl pyridine were dissolved in dimethylformamide and AIBN added. The reactants were then mixed and the polymerisation was then carried out under a nitrogen atmosphere in a water bath at 333±0.1K for the required number of hours. The polymer was precipitated into petroleum ether 40-60. This was then redissolved in chloroform and reprecipitated in petroleum ether 40-60, this procedure was repeated four times. The purified products were dried in vacuo at 353K. Characterisation was performed using ¹H nmr, GPC and membrane osmometry.

3.5 SYNTHESIS OF STATISTICAL COPOLYMERs

The comonomer and AIBN were weighed accurately into a round bottom flask and dimethylformamide added. The reactants were then dissolved and the polymerisation was carried out under an
atmosphere of nitrogen in a water bath at 333±0.1K for the required number of hours. The polymer was precipitated into petroleum ether 40-60. This was then redissolved in chloroform and reprecipitated in petroleum ether 40-60, this procedure was repeated four times. The purified products were dried in vacuo at 353K. Characterisation was performed using $^1$H nmr.

3.6 SYNTHESIS OF GRAFT COPOLYMERS

The comonomer, macromonomer and AIBN were weighed accurately into a round bottom flask and dimethylformamide added. The reactants were then mixed and the polymerisation was carried out under an atmosphere of nitrogen in a water bath at 333±0.1K for the required number of hours. The polymer was precipitated into petroleum ether 40-60. This was then redissolved in chloroform and reprecipitated in petroleum ether 40-60, this procedure was repeated four times. The purified products were dried in vacuo at 353K. Characterisation was performed using $^1$H nmr, GPC and membrane osmometry.

Homopolymer contamination was assessed for graft copolymers where a low level of grafting was predicted. For copolymerisations involving vinyl pyridine, the purified products were stirred with 0.5M hydrochloric acid for 24 hours after which time the solution was decanted off and the graft copolymer washed with 1M sodium hydroxide solution. Pyrrolidone containing copolymers were dissolved in DMF and added to a five fold excess methanol with sodium chloride (5g). Deionised water was then added until the graft copolymer precipitated. Further fractions containing a lower proportion of graft copolymer were obtained by adding more water. The final fraction contained nearly pure homopolymer. $^1$H nmr spectroscopy was repeated on the extracted graft copolymers.

3.6.1 "Blank" Copolymerisations using uncapped polystyrene

A "blank" experiment was performed using polystyrene without a styryl end group (i.e. no copolymerisations should be observed). The reaction conditions were identical to
macromonomer copolymerisations. Products were analysed by \(^1\)H nmr to assess the possibility of transfer grafting reactions onto the polystyrene segments.

3.7 DETERMINATION OF REACTIVITY RATIOS

Reactivity ratios were obtained for all copolymerisations by evaluating the data obtained at low conversion. The Finnemann-Ross\(^1\) and Kelen-Tudos\(^2\) linear least squares methods and Jaack's simplification\(^3\), as described in section 2.6.4 were used to assess each series of copolymerisations and obtain estimates of the reactivity ratios.

3.8 THE SYNTHESIS OF NON-AQUEOUS DISPERSIONS

A number of different polymer dispersions have been made.

3.8.1 The Preparation of Non-aqueous Dispersions of Polyethylene terephthalate

The dispersion apparatus shown in figure 3.3 was used. Bis-hydroxyethyl terephthalate (BHET), graft copolymer stabiliser and manganese II acetate tetrahydrate were added to tetraisobutane 90. This was then purged and sparged with nitrogen throughout the polymerisation. The reaction flask was heated to 433K at which point the BHET had melted and was emulsified using a mechanical stirrer at a speed of 600 revolutions per minute. The reaction flask was further heated to 513K with evolution of ethylene glycol. This was removed by the Dean-Stark apparatus. The overhead temperature was monitored to observe the complete removal of ethylene glycol, this was complete after about 20 minutes. The polymerisation was then continued for a further 5 hours, thereby increasing the molar mass.

After the polymerisation was complete, the heater was turned off but the flask was continued to be stirred until cool. The polymer was then filtered off and washed with petroleum ether 40-60. The residual stabiliser was removed by washing with dichloromethane. The polymer dispersion was then dried in vacuo over night. Characterisation was performed using scanning
FIGURE 3.3
REACTOR FOR NON-AQUEOUS DISPERSION POLYMERISATIONS
OF BIS-HYDROXY(ETHYL TEREPTHALATE)
electron microscopy (SEM), dynamic scanning calorimetry (DSC) and GPC in o-chlorophenol at 403K by ICI Wilton Materials Research Centre.

3.8.2 The Preparation of Micellar Dispersions

Micellar dispersions have been prepared with graft copolymers in the G11, G12 and G14 series. Four different dispersion media were employed: cyclohexane, toluene and methanol and oligostyrene ($M_n = 580$). The graft copolymer (0.3g) was first dissolved in dichloromethane (5.0g). This solution was then added dropwise with stirring to the dispersion solvent (10.5g). The dichloromethane was then removed by warming the dispersion.

3.8.3 The Free-Radical Non-aqueous Dispersion Polymerisation of Methyl Methacrylate

Dispersions of PMMA in cyclohexane were prepared using the graft copolymers as steric stabilisers. The dispersion polymerisations were performed using the apparatus shown in figure 3.4. Purified MMA monomer, AIBN initiator and graft copolymer were dissolved in cyclohexane. A nitrogen blanket was used throughout the experiment and the polymerisation temperature was thermostatically controlled to 343±0.1K by immersing the reactor in a water bath.

A number of reaction parameters were varied in order to investigate the polymerisation, these included stabiliser concentration and composition, the use of a "seed" stage and altering the monomer and initiator concentration.

3.8.4 The Free-Radical Non-aqueous Dispersion Polymerisation of Styrene

Dispersion of polystyrene in methanol were prepared using all the graft copolymers and homopolymers as steric stabilisers. The dispersion polymerisations were performed using the apparatus shown in figure 3.4. Purified styrene monomer, AIBN initiator and stabiliser were dissolved in methanol. A nitrogen blanket was used throughout the experiment and the polymerisation temperature was controlled to 338±0.1K by
FIGURE 3.4
APPARATUS USED FOR NON-AQUEOUS DISPERSION POLYMERISATIONS
OF MMA, STYRENE AND VINYL PYRRODINE
immersing the reactor in a thermostatically controlled water bath. A number of reaction parameters were varied in order to investigate the polymerisation.

3.8.5 The Free-Radical Non-aqueous Dispersion Polymerisation of 4-Vinyl Pyridine

Dispersions of poly(4-vinyl pyridine) in either cyclohexane or toluene were prepared using poly(2-vinyl pyridine)-graft polystyrene and poly(4-vinyl pyridine)-graft-polystyrene as stabilisers. The same procedure as in section 3.8.3 was adopted.

3.8.6 Determination of the Extent of Conversion

Monomer conversion was determined at the end of the polymerisation for each of the dispersion polymerisation systems. A known amount of dispersion was added to a pre-weighed small vessel. Unpolymerised monomer and diluent were allowed to evaporate under vacuum at room temperature to a constant weight. By comparison with the total solids content before polymerisation and taking account of the small loss of material due to evaporation during polymerisation, the monomer conversion can be determined.

3.8.7 Purification of Non-aqueous Dispersions by Redispersion

In order to remove unconverted monomer, unadsorbed stabiliser and initiator residues from the dispersions prepared, each dispersion was subjected to several redispersion cycles. The dispersions were centrifuged at 20000 rpm for 15 minutes and the supernatant above the sedimented particles replaced with fresh dispersion medium. The particles were redispersed by vigorous shaking and the redispersion cycle repeated. Analysis of the supernatant showed that 3 or 4 such redispersion were usually sufficient to remove the excess stabiliser content to negligible proportions.
3.9 CHARACTERISATION PROCEDURES

3.9.1 Macromonomer Characterisation

GPC and $^1$H nmr spectroscopy were used to characterise the macromonomers.

3.9.1.1 Gel Permeation Chromatography (GPC)

Polymers were initially dissolved in THF (concentration approximately 0.2% w/v) and spiked with toluene as an internal standard. This solution was loaded into a 6-port injection valve containing a 50μl loop. The solutions were injected onto the column fitted with a 2μm pre-filter. The polymers were eluted with tetrahydrofuran at room temperature using a Knauer High Performance Liquid Chromatography Pump 64 at a flow rate of 1.0ml per minute. Detection was carried out using a Knauer differential refractometer detector connected to a JJ chart recorder, set with a chart speed of 10mm per minute. Two columns obtained from Polymer Laboratories Ltd were used in series: they both contained polystyrene gels with a particle size of 5 μm, the first had a pore size of 500Å, the other 100Å. The columns were calibrated with narrow molar mass distribution polystyrene standards (Polymer Laboratories). By taking the injection point as zero elution volume and the toluene peak as complete elution, the polymer standard elution volumes were expressed as a percentage of the internal standard elution volume. The chromatograms of the polymer samples were analysed by dividing the chromatographic curves into a series of trace heights and elution volumes, again expressed as a percentage of the total elution volume of the internal standard. A computer program by Croucher$^{178}$ was used to calculate the molar mass averages from the chromatograms. Values obtained for the number average molar mass ($M_n$) and weight average molar mass ($M_w$) were not corrected for peak broadening and the polydispersity index represents a maximum value.
3.9.1.2 Nuclear Magnetic Spectroscopy (\( ^1H \) nmr)

\( ^1H \) nmr spectroscopy was used to determine macromonomer composition. Samples were submitted to the departmental spectroscopy service for analysis. The samples were dissolved in deuteriated chloroform (20mg/ml) containing tetramethylsilane (TMS) at a concentration of 15\( \mu L/100mL \). Spectra were obtained using a Bruker 250 MHz spectrometer. Analysis of the integrations of the initiator and end group fragments gave information on functionality. Comparison of the polystyrene constitutional repeat unit (CRU) with the initiator fragment was used to determine polymer molar masses.

3.9.2 Graft Copolymer Characterisation

The graft copolymers were characterised using GPC in DMF, membrane osmometry and \( ^1H \) nmr. The homopolymer backbones and statistical copolymers were also analysed using these techniques.

3.9.2.1 Gel Permeation Chromatography in DMF (GPC)

Polymers were initially dissolved in DMF with 0.1\% by wt LiBr (concentration approximately 0.2\% w/v) and spiked with dimethylsulphoxide as an internal standard. This solution was loaded into a 6-port injection valve containing a 200\( \mu L \) loop. The solutions were injected onto the column fitted with a 2\( \mu m \) pre-filter. The polymers were eluted with DMF using a Waters series 600 HPLC pump at a flow rate of 1.0ml per minute. Detection was carried out using a Knauer differential refractometer connected to a JJ chart recorder, set with a chart speed of 10mm per minute. A column obtained from Polymer Laboratories Ltd was used with a 10\( \mu m \) particle size and a mixed bed. The columns were calibrated with narrow molar mass distribution polyethylene oxide standards (Toya Soda Japan Ltd). By taking the injection point as zero elution volume and the toluene peak as complete elution, the polymer standard elution volumes were expressed as a percentage of the internal standard elution volume. The chromatograms of the polymer
samples were analysed by dividing the chromatographic curves into a series of trace heights and elution volumes, again expressed as a percentage of the total elution volume of the internal standard. A computer program\(^{178}\) was used to calculate the molar mass averages from the chromatograms. Values obtained for the number average molar mass (\(M_n\)) and weight average molar mass (\(M_w\)) were not corrected for peak broadening and the polydispersity index represents a maximum value.

3.9.2.2 Nuclear Magnetic Spectroscopy (\(^1\)H nmr)

\(^1\)H nmr spectroscopy was used to determine polymer compositions. Samples were submitted to the departmental spectroscopy service for analysis. The samples were dissolved as in section 3.9.1.2 and analysed using a Bruker 250 MHz spectrometer. Comparison of the integrations of the styrene CRU to the comonomer CRU enabled compositions to be determined.

3.9.2.3 Membrane Osmometry

The number average molar masses of the copolymers and homopolymer backbones was determined by high speed membrane osmometry. A Hewlett-Packard 502 instrument was used as described in the instruction manual at 308K with DMF (0.1M LiBr added) as the solvent. The osmotic pressure (\(\pi\)) of a series of polymer solutions at concentrations 1-10 g.L\(^{-1}\) were measured for each sample.

3.9.2.4 Thermal Analysis

Dynamic scanning calorimetry (DSC) was performed on a Perkin Elmer series 4 DSC to assess glass transition temperatures and microphase separation. Samples were heated from 313K to 473K at 10K/min. Dynamic mechanical thermal analysis (DMTA) was also performed. The instrument was a Polymer Laboratories standard head model using a small clamping frame and flat face spreader with a frequency of 1Hz and a strain x4. The samples were pressed at 6 tonnes for 1 minute at 423K between whatman filter paper, they were heated from 303K to 473K at 2K/min. Data can
be analysed for miscibility between the microphases in the bulk graft copolymer.

3.9.3 Characterisation of Non-aqueous Dispersions

The polymer dispersions were characterised using a number of techniques. The particle size, shape and distribution was analysed using electron microscopy. Surface coverage was determined using UV-Vis and $^1$H nmr spectroscopy. SANS was used to determine micelle size and fringe thicknesses.

3.9.3.1 Transmission Electron Microscopy (TEM)

TEM was used extensively to characterise micellar and polymer dispersions. Samples were prepared by placing a few drops of dilute dispersion (approx. 0.1% (w/v) polymer content) directly onto a carbon-coated copper grid and evaporating to dryness. Samples were examined at magnifications of 2-160×10^3 times using a JEOL JEM 100CX electron microscope calibrated with a replica of a 2160 lines mm^-1 grating and operating with a 60KV accelerating voltage. Typically 3-4 micrographs were taken for each sample from different parts of the grid. Particle size and size distribution were calculated from direct measurement of individual particles on the micrographs.

3.9.3.2 Scanning Electron Microscopy (SEM)

SEM was used to characterise the PET particles which were too large for the TEM. Wood glue adhesive was used to stick the particles onto the stud. Other non-aqueous dispersions were prepared by dropping a few drops of dilute dispersion directly onto a glass cover slip stuck to a stud. These were then placed in a vacuum coating machine and coated with gold. Samples were examined using a Leica Cambridge stereoscan 360 electron microscope and operating at 10kV accelerating voltage. SEM is a useful tool for examining surface morphology.

3.9.3.3 Surface Coverage

(i) $^1$H nmr spectroscopy
Samples of dispersions were purified by redispersion cycles and then evaporated to dryness under vacuum before dissolving in deuteriated chloroform and analysed in a similar manner to section 3.9.2.2. By comparison of the vinyl pyridine CRU to the polystyrene CRU from the dispersion it was possible to determine surface coverage.

(ii) UV-Vis spectroscopy

From a suitable calibration of the UV absorbance of a group in a compound, the concentration of groups can be determined quantitatively according to the Beer-Lambert law.

Purified and dried PMMA dispersion samples were analysed for poly(2-vinyl pyridine)-graft-polystyrene and poly(4-vinyl pyridine)-graft-polystyrene stabiliser content from the UV absorption of the aromatic units in the copolymer using a Shimadzu UV 160 UV-Vis spectrometer. The constant was determined by setting up a calibration curve of absorbance versus concentration with solutions of the same graft copolymer. Absorbance values were obtained at 280nm and a calibration curve plotted (see figure 3.5). Solutions of dried dispersion were then prepared accurately in chloroform (typically 4.0mg.cm\(^{-3}\)) and the UV spectra measured. From the calibration curve it is possible to determine the concentration of graft copolymer stabiliser.

3.9.3.4 Small-Angle X-Ray Scattering

A Rigaku Denki camera (No. 2202) with slit collimation and counter detector was employed for all SAXS work. The X-Ray source operated at 40kV and 20mA with nickel filtered CuK\(_\alpha\) radiation. The nickel filter selectively removed the CuK\(_\beta\) radiation. The detector was a Nuclear Enterprise DMI-2 beryllium windowed scintillation detector (sodium iodide activated with thallium). Identical instrument set up and data logging to Redford\(^{179}\) was used. Micellar dispersions were filtered to remove dust and then introduced into the Lindemann
FIGURE 3.5
CALIBRATION CURVE OF ABSORBANCE (280nm) VERSUS CONCENTRATION FOR G11D

ACs...om...Q...

0.5
0.4
0.3
0.2
0.1
0.0

0.000 0.002 0.004 0.006 0.008 0.010 0.012

concentration (g/ml)
glass capillary tubes (2mm diameter). The tube tops were sealed using a small bunsen flame.

Samples were placed in the camera in an ambient temperature sample holder. All samples were scanned over the range of 0.06° to 1.05° or 2.05° in increments of 0.01°. Counts were made over 300 seconds at each position. After scanning each sample, the tube was replace with an identical one containing pure solvent and scanned over the complete angular range. This background count was subtracted from the sample count before processing.

The scattered data with background data subtracted were plotted against 2θ and smoothed using a cubic Savitsky-Golay function. In order to carry out the desmearing of the data the curve was fitted to a fourier series. The data for the region 0° to 0.06° was estimated because of the experimental difficulties of obtaining data in such close proximity to the primary X-ray beam. It is difficult to model curves with large gradients at its extremities using fourier series, therefore the curve was smoothed over to give a gradient close to zero at 0°. The desmearing program was a fortran program supplied by Vonk. Approximately 30 to 40 terms of the fourier series were required to model the scattering curves.
4. RESULTS

4.1 CHARACTERISATION OF POLYSTYRENE MACROMONOMERS

Styryl-capped polystyrene macromonomers were characterised using the following techniques, and the results summarised in table 4.1.

4.1.1 Nuclear Magnetic Resonance Spectroscopy

The chemical shifts due to different protons in the macromonomer are given in table 4.2. By comparison of the integration of $H_A$ of the methyl protons present in the sec-butyl initiator fragment at $\delta = 0.5-0.9$ ppm and the aromatic protons ($H_E$) at $\delta = 6.0-7.0$ ppm, it is possible to obtain the average number ($x$) of styrene repeat units per chain. The aromatic protons due to the diphenylethylene unit must be accounted for prior to calculating the number of repeat units. Therefore,

$$x = \frac{(H_A - (H_E / 6) \cdot 10)}{H_E / 6}$$  \hspace{1cm} (4.1)

The functionality $f$, can be calculated in a similar manner by comparison of the initiator fragment as before ($H_A$) with the methylene protons bridging the styryl endgroup ($H_C$) and the diphenyl group. Therefore,

$$f = \frac{H_C / 2}{H_E / 6}$$  \hspace{1cm} (4.2)

The olefinic protons in the styrene endgroup $\delta = 5.0-6.0$ ppm could also be used but some overlap with the aromatic protons may be occurring.

4.1.2 Gel Permeation Chromatography

The polydispersity of the macromonomer will be a maximum value as no account has been taken of peak broadening effects;
<table>
<thead>
<tr>
<th>Code</th>
<th>End Group</th>
<th>$M_n$</th>
<th>$M_w$</th>
<th>$M_md$</th>
<th>$M_n$</th>
<th>% functionality</th>
</tr>
</thead>
<tbody>
<tr>
<td>M4</td>
<td>DPE</td>
<td>4.65</td>
<td>5.23</td>
<td>1.13</td>
<td>3.79</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td>VBC</td>
<td>4.53</td>
<td>5.13</td>
<td>1.13</td>
<td>3.60</td>
<td>97</td>
</tr>
<tr>
<td>M5</td>
<td>DPE</td>
<td>3.25</td>
<td>4.03</td>
<td>1.24</td>
<td>3.71</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td>VBC</td>
<td>3.27</td>
<td>4.06</td>
<td>1.24</td>
<td>3.17</td>
<td>94</td>
</tr>
<tr>
<td>M6</td>
<td>DPE</td>
<td>2.61</td>
<td>3.04</td>
<td>1.17</td>
<td>2.80</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td>VBC</td>
<td>2.81</td>
<td>3.35</td>
<td>1.19</td>
<td>3.12</td>
<td>90</td>
</tr>
</tbody>
</table>

NB Capping Agent: DPE = diphenylethylen VBC = vinylbenzyl chloride
Molar Masses in kg/mol
<table>
<thead>
<tr>
<th>$\delta$ ppm</th>
<th>Assignment</th>
<th>Label in Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>.55 -.90</td>
<td>methyl protons from sec-butyl fragment</td>
<td>A</td>
</tr>
<tr>
<td>.90 - 2.6</td>
<td>CH$_2$ and CH protons on PS backbone</td>
<td>B</td>
</tr>
<tr>
<td>3.1 - 3.4</td>
<td>CH$_2$ protons bridging styryl group and diphenyl unit</td>
<td>C</td>
</tr>
<tr>
<td>4.9 - 6.2</td>
<td>-C=C-H protons</td>
<td>D</td>
</tr>
<tr>
<td>6.2 - 7.4</td>
<td>Aromatic protons</td>
<td>E</td>
</tr>
<tr>
<td>3.5</td>
<td>diphenyl substituted -CH proton</td>
<td>F</td>
</tr>
</tbody>
</table>

\[ \text{Structure Diagram} \]
this may also effect $M_n$ and $M_w$ values slightly. No significant increase in polydispersity is observed after endcapping. Therefore, no side reactions on addition of vinylbenzyl chloride occur. The GPC column was calibrated with a range of low molar mass polystyrene standards. Therefore, the molar masses derived for the macromonomers can be considered to be very close to the absolute values. This assumes that the size of the diphenyl and styrene endgroups are not significantly different from styryl chain ends in the polystyrene standards. Comparison of the $M_n$ values obtained by GPC and $^1$H nmr in table 4.1 show a reasonable correlation between the two methods.

4.2 CHARACTERISATION OF N-(VINYL BENZYL) PYRROLIDONE

$^1$H nmr, IR and mass spectrometry were performed on the purified monomer. Table 4.3 shows the chemical shifts of the protons and carbon atoms and table 4.4 lists the infra-red peaks and primary ion found by mass spectroscopy. The chemical shifts observed in the nmr show the presence of a 60:40 mixture of meta and para isomers. The vinyl benzyl chloride used as a starting material contained the same ratio of isomers. The primary ion was also found in the mass spectrum and correlated with the expected mass.

4.3 CHARACTERISATION OF STATISTICAL COPOLYMERS

The copolymerisations were carried to low conversions in order to determine the reactivity ratios. The copolymer compositions were determined by $^1$H nmr. Tables 4.5 & 4.6 contain data on the copolymerisations.

4.4 CHARACTERISATION OF THE GRAFT COPOLYMERS

The graft copolymer stabilisers were characterised by $^1$H nmr, GPC and membrane osmometry. Tables 4.7, 4.8 & 4.9 contain data on the graft copolymer molar masses and compositions. Table 4.10 details data for the homopolymers.

In order to establish that the macromonomers copolymerised through the terminal double bond and not by transfer reactions
**TABLE 4.3**

1H AND 13C NMR CHEMICAL SHIFT ASSIGNMENTS FOR N-(VINYLBENZYL)PYRROLIDONE

<table>
<thead>
<tr>
<th>ppm</th>
<th>1H nmr Coupling Constant</th>
<th>Assignment</th>
<th>Label in Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.00 (q)</td>
<td>2.00 Hz</td>
<td>-CH2-</td>
<td>A</td>
</tr>
<tr>
<td>2.45 (t)</td>
<td>2.45 Hz</td>
<td>-CH2-C=O</td>
<td>B</td>
</tr>
<tr>
<td>3.26 (t)</td>
<td>3.26 Hz</td>
<td>-CH2-N-C=O</td>
<td>C</td>
</tr>
<tr>
<td>4.40 (s)</td>
<td>4.40 Hz</td>
<td>Ph-CH2-N</td>
<td>D</td>
</tr>
<tr>
<td>5.26 (dd)</td>
<td>5.26 Hz</td>
<td>2 &amp; 17</td>
<td>C=CH-H</td>
</tr>
<tr>
<td>5.74 (dd)</td>
<td>5.74 Hz</td>
<td>2 &amp; 17</td>
<td>C=CH-H</td>
</tr>
<tr>
<td>6.70 (dd)</td>
<td>6.70 Hz</td>
<td>17 &amp; 11</td>
<td>C=CH-H</td>
</tr>
<tr>
<td>7.29 (m)</td>
<td>7.29 Hz</td>
<td>Aromatic</td>
<td>E</td>
</tr>
</tbody>
</table>

**13C nmr**

<table>
<thead>
<tr>
<th>ppm</th>
<th>Assignment</th>
<th>Label in Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>17.6</td>
<td>-CH2-</td>
<td>A</td>
</tr>
<tr>
<td>30.8</td>
<td>-CH2-C=O</td>
<td>B</td>
</tr>
<tr>
<td>46.3</td>
<td>-CH2-N</td>
<td>C</td>
</tr>
<tr>
<td>114.0</td>
<td>Ph-CH2-N</td>
<td>E</td>
</tr>
<tr>
<td>127</td>
<td>Aromatic</td>
<td>F</td>
</tr>
<tr>
<td>137</td>
<td>C=CH-H</td>
<td>G</td>
</tr>
<tr>
<td>174.7</td>
<td>C=O</td>
<td>D</td>
</tr>
<tr>
<td>IR cm⁻¹</td>
<td>Assignment</td>
<td></td>
</tr>
<tr>
<td>---------</td>
<td>--------------------------</td>
<td></td>
</tr>
<tr>
<td>3084</td>
<td>aromatic C-H stretch</td>
<td></td>
</tr>
<tr>
<td>2975</td>
<td>saturated C-H stretch</td>
<td></td>
</tr>
<tr>
<td>1684</td>
<td>lactam C=O stretch</td>
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</tr>
<tr>
<td>1603</td>
<td>aromatic C=C stretch</td>
<td></td>
</tr>
<tr>
<td>1490</td>
<td>aromatic C=C stretch</td>
<td></td>
</tr>
<tr>
<td>1428</td>
<td>C-H deformation</td>
<td></td>
</tr>
</tbody>
</table>

Mass Spectrum
Measured Mass=201.1147  Expected Mass=201.1156
(-.69mmu, -3.4ppm)
TABLE 4.5
SYNTHESIS AND CHARACTERISATION OF POLY(2-VP)-CO-PS

<table>
<thead>
<tr>
<th>Code</th>
<th>Conversion(^2)</th>
<th>Wt fraction styrene feed(^3)</th>
<th>Copolymer(^4)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C9A</td>
<td>2.3</td>
<td>0.10</td>
<td>0.13</td>
</tr>
<tr>
<td>C9B</td>
<td>2.7</td>
<td>0.31</td>
<td>0.26</td>
</tr>
<tr>
<td>C9C</td>
<td>1.5</td>
<td>0.50</td>
<td>0.43</td>
</tr>
<tr>
<td>C9D</td>
<td>1.0</td>
<td>0.69</td>
<td>0.63</td>
</tr>
</tbody>
</table>

SYNTHESIS AND CHARACTERISATION OF POLY(4-VP)-CO-PS

<table>
<thead>
<tr>
<th>Code</th>
<th>Conversion(^2)</th>
<th>Wt fraction styrene feed(^3)</th>
<th>Copolymer(^4)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C10A</td>
<td>4.2</td>
<td>0.127</td>
<td>0.101</td>
</tr>
<tr>
<td>C10B</td>
<td>4.4</td>
<td>0.313</td>
<td>0.248</td>
</tr>
<tr>
<td>C10C</td>
<td>3.5</td>
<td>0.514</td>
<td>0.353</td>
</tr>
<tr>
<td>C10D</td>
<td>4.8</td>
<td>0.701</td>
<td>0.574</td>
</tr>
</tbody>
</table>

NB.
1 Polymerisation time 1 hour at 333K. Total [Monomer]=20% w/v in DMF. [AIBN]=2.5% w/w on monomer.
2 Determined gravimetrically.
3 Determined gravimetrically, weight fraction based on monomer.
4 Determined by \(^1\)H nmr.
**TABLE 4.6**
SYNTHESIS AND CHARACTERISATION OF POLY(VBP)-CO-PS¹

<table>
<thead>
<tr>
<th>Code</th>
<th>Conversion²</th>
<th>Wt. fraction styrene feed³</th>
<th>Wt. fraction styrene Copolymer⁴</th>
</tr>
</thead>
<tbody>
<tr>
<td>C16A</td>
<td>11.5%</td>
<td>.20</td>
<td>.23</td>
</tr>
<tr>
<td>C16B</td>
<td>6%</td>
<td>.47</td>
<td>.48</td>
</tr>
<tr>
<td>C16C</td>
<td>6%</td>
<td>.65</td>
<td>.64</td>
</tr>
<tr>
<td>C16D</td>
<td>5%</td>
<td>.82</td>
<td>.81</td>
</tr>
</tbody>
</table>

NB.
1 Polymerisation time 4 hours at 333K. Total [Monomer]=20% w/v in DMF. [AIBN]=1% w/w on monomer.
2 Determined gravimetrically.
3 Determined gravimetrically, weight fraction based on monomer.
4 Determined by ^1^H nmr.
TABLE 4.7
SYNTHESIS AND CHARACTERISATION OF POLY(4-VP)-GRAFT-PS

<table>
<thead>
<tr>
<th>Code</th>
<th>Type</th>
<th>Macromonomer</th>
<th>%Wt</th>
<th>Feed</th>
<th>Copolymer Wt. fraction</th>
<th>Mac</th>
<th>Conversion</th>
<th>( M_n )</th>
<th>( M_w )</th>
<th>( M_{md} )</th>
<th>( M_n )</th>
<th>( N_g )</th>
</tr>
</thead>
<tbody>
<tr>
<td>G4A</td>
<td>M4</td>
<td>3.6</td>
<td>14</td>
<td>.13</td>
<td>.063</td>
<td>15.9</td>
<td>29.6</td>
<td>1.86</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>G4B</td>
<td>M4</td>
<td>3.6</td>
<td>9</td>
<td>.26</td>
<td>.15</td>
<td>16.6</td>
<td>29.6</td>
<td>1.78</td>
<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>G4C</td>
<td>M4</td>
<td>3.6</td>
<td>11</td>
<td>.37</td>
<td>.20</td>
<td>14.5</td>
<td>29.4</td>
<td>2.03</td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>G4D</td>
<td>M4</td>
<td>3.6</td>
<td>6</td>
<td>.52</td>
<td>.27</td>
<td>10.2</td>
<td>20.9</td>
<td>2.05</td>
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<td>G5A</td>
<td>M4</td>
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<td>75</td>
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<td>.087</td>
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<td>26.2</td>
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<td>.17</td>
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<td>11.6</td>
<td>2.04</td>
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<td>G11A</td>
<td>M4</td>
<td>3.6</td>
<td>53</td>
<td>.26</td>
<td>.15</td>
<td>15.9</td>
<td>29.2</td>
<td>1.83</td>
<td></td>
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<tr>
<td>G11A*</td>
<td>M4</td>
<td>3.6</td>
<td>53</td>
<td>.26</td>
<td>.16</td>
<td>15.9</td>
<td>29.2</td>
<td>1.83</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>G11B</td>
<td>M4</td>
<td>3.6</td>
<td>44</td>
<td>.50</td>
<td>.36</td>
<td>12.2</td>
<td>23.9</td>
<td>1.96</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>G11C</td>
<td>M4</td>
<td>3.6</td>
<td>46</td>
<td>.62</td>
<td>.46</td>
<td>11.4</td>
<td>21.3</td>
<td>1.87</td>
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<td>M4</td>
<td>3.2</td>
<td>45</td>
<td>.75</td>
<td>.68</td>
<td>10.7</td>
<td>21.5</td>
<td>2.00</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

1 Polymerisation time G4=2 hours G5=24 hours G11=18 hours at 333K total [Monomer]=20% w/v in DMF. [AIBN]=2.5% (w/w) on monomer for G4 & G5, [AIBN]=1.0% (w/w) on monomer for G11.

2 GPC in DMF+0.1%wt LiBr molar masses kg.mol\(^{-1}\)

3 MO = Membrane Osmomtrity molar masses kg.mol\(^{-1}\)

4 \( N_g \) = average number of grafts per molecule

Mac = Macromonomer * = purified by homopolymer removal
TABLE 4.8
SYNTHESIS AND CHARACTERISATION OF POLY(2-VP)-GRAFT-PS

<table>
<thead>
<tr>
<th>Code</th>
<th>Macromonomer</th>
<th>Type</th>
<th>Mₙ</th>
<th>%Wt</th>
<th>Conversion</th>
<th>Feed</th>
<th>Copolymer</th>
<th>Wt.fraction Mac</th>
<th>Mₙ</th>
<th>Mₘ</th>
<th>Mmd</th>
<th>GPC²</th>
<th>MO³</th>
<th>Ng</th>
</tr>
</thead>
<tbody>
<tr>
<td>G6A</td>
<td>M₄</td>
<td>3.6</td>
<td>6</td>
<td>0.15</td>
<td>0.077</td>
<td>6.1</td>
<td>12.2</td>
<td>2.00</td>
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</tr>
<tr>
<td>G6B</td>
<td>M₄</td>
<td>3.6</td>
<td>5</td>
<td>0.31</td>
<td>0.19</td>
<td>6.6</td>
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<td>1.98</td>
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<tr>
<td>G6C</td>
<td>M₄</td>
<td>3.6</td>
<td>6</td>
<td>0.40</td>
<td>0.26</td>
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<td>1.90</td>
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<tr>
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<td>M₄</td>
<td>3.6</td>
<td>8</td>
<td>0.54</td>
<td>0.35</td>
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<td>10.6</td>
<td>2.03</td>
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<td>G7A</td>
<td>M₄</td>
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<td>54</td>
<td>0.13</td>
<td>0.097</td>
<td>8.1</td>
<td>15.4</td>
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<td>M₄</td>
<td>3.6</td>
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<td>0.29</td>
<td>0.18</td>
<td>5.9</td>
<td>12.3</td>
<td>2.09</td>
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<td>M₄</td>
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<td>0.33</td>
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<td>11.1</td>
<td>2.02</td>
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<td>3.2</td>
<td>40</td>
<td>0.25</td>
<td>0.17</td>
<td>10.9</td>
<td>19.9</td>
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<td></td>
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</tr>
<tr>
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<td>M₅</td>
<td>3.2</td>
<td>40</td>
<td>0.25</td>
<td>0.22</td>
<td>10.9</td>
<td>19.9</td>
<td>1.82</td>
<td>25.9</td>
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<td></td>
<td></td>
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<td>15.3</td>
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<td></td>
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<tr>
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<td>M₅</td>
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<td>0.63</td>
<td>0.52</td>
<td>7.6</td>
<td>15.0</td>
<td>1.96</td>
<td>31.0</td>
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<td></td>
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<td>5.1</td>
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<tr>
<td>G12D</td>
<td>M₅</td>
<td>3.2</td>
<td>32</td>
<td>0.74</td>
<td>0.66</td>
<td>6.2</td>
<td>13.0</td>
<td>2.12</td>
<td>29.5</td>
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<td></td>
<td></td>
<td></td>
<td>6.1</td>
</tr>
</tbody>
</table>

1 Polymerisation time G6=2 hours G7=18 hours G11=18 hours at 333K total [Monomer]=20% w/v in DMF. [AIBN]=2.5% (w/w) on monomer for G6 & G7, [AIBN]=1.0% (w/w) on monomer for G12.
2 GPC in DMF+0.1%wt LiBr molar masses kg.mol⁻¹
3 MO = Membrane Osmometry molar masses kg.mol⁻¹
4 Ng = average number of grafts per molecule
* = purified by homopolymer removal
**TABLE 4.9**

SYNTHESIS AND CHARACTERISATION OF POLY(VBP)-GRAFT-PS\(^1\)

<table>
<thead>
<tr>
<th>Code</th>
<th>Type</th>
<th>Mn</th>
<th>%Wt Conversion</th>
<th>Feed Wt. fraction Mac</th>
<th>Copolymer Mac</th>
<th>M(_n)</th>
<th>M(_w)</th>
<th>Mmd</th>
<th>M(_n) MO3</th>
<th>Ng</th>
</tr>
</thead>
<tbody>
<tr>
<td>G13A</td>
<td>M6</td>
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<td>15</td>
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<td></td>
<td>15.9</td>
<td>28.9</td>
<td>1.82</td>
<td></td>
<td></td>
</tr>
<tr>
<td>G13B</td>
<td>M6</td>
<td>3.1</td>
<td>13</td>
<td>.39 .32</td>
<td></td>
<td>13.3</td>
<td>27.0</td>
<td>2.03</td>
<td></td>
<td></td>
</tr>
<tr>
<td>G13C</td>
<td>M6</td>
<td>3.1</td>
<td>12</td>
<td>.59 .53</td>
<td></td>
<td>11.1</td>
<td>23.5</td>
<td>2.12</td>
<td></td>
<td></td>
</tr>
<tr>
<td>G13D</td>
<td>M6</td>
<td>3.1</td>
<td>11</td>
<td>.80 .76</td>
<td></td>
<td>7.4</td>
<td>15.5</td>
<td>2.10</td>
<td></td>
<td></td>
</tr>
<tr>
<td>G14A</td>
<td>M6</td>
<td>3.1</td>
<td>64</td>
<td>.20 .15</td>
<td></td>
<td>14.0</td>
<td>26.2</td>
<td>1.87</td>
<td></td>
<td></td>
</tr>
<tr>
<td>G14A*</td>
<td>M6</td>
<td>3.1</td>
<td>64</td>
<td>.20 .17</td>
<td></td>
<td>14.0</td>
<td>26.2</td>
<td>1.87</td>
<td>39.0</td>
<td>2.1</td>
</tr>
<tr>
<td>G14B</td>
<td>M6</td>
<td>3.1</td>
<td>56</td>
<td>.43 .36</td>
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<td>12.3</td>
<td>25.2</td>
<td>2.05</td>
<td>39.0</td>
<td>4.5</td>
</tr>
<tr>
<td>G14C</td>
<td>M6</td>
<td>3.1</td>
<td>52</td>
<td>.60 .56</td>
<td></td>
<td>7.8</td>
<td>16.6</td>
<td>2.13</td>
<td>39.0</td>
<td>7.6</td>
</tr>
<tr>
<td>G14D</td>
<td>M6</td>
<td>3.1</td>
<td>44</td>
<td>.80 .78</td>
<td></td>
<td>5.4</td>
<td>11.3</td>
<td>2.09</td>
<td>39.2</td>
<td>9.8</td>
</tr>
</tbody>
</table>

1 Polymerisation time G13=6 hours G14=30 hours at 333K
   total [Monomer]=20% w/v in DMF. [AIBN]=1.0% (w/w) on monomer.
2 GPC in DMF + 0.1%wt LiBr molar masses kg.mol\(^{-1}\)
3 MO = Membrane Osmometry molar masses kg.mol\(^{-1}\)
4 \(N_g\) = average number of grafts per molecule
* = purified by homopolymer removal
### TABLE 4.10
SYNTHESIS AND CHARACTERISATION OF HOMOPOLYMER BACKBONES

<table>
<thead>
<tr>
<th>Code</th>
<th>%wt Conversion</th>
<th>%wt [I]$^2$</th>
<th>$M_n$</th>
<th>$M_w$</th>
<th>$M_{md}$</th>
<th>$M_n$ $^4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Poly(4-VP)A</td>
<td>62</td>
<td>1</td>
<td>16.1</td>
<td>31.2</td>
<td>1.94</td>
<td>35.3</td>
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<tr>
<td>Poly(4-VP)B</td>
<td>70</td>
<td>2.5</td>
<td></td>
<td></td>
<td></td>
<td>26.3</td>
</tr>
<tr>
<td>Poly(4-VP)C</td>
<td>55</td>
<td>.05</td>
<td></td>
<td></td>
<td></td>
<td>69.0</td>
</tr>
<tr>
<td>Poly(2-VP)</td>
<td>35</td>
<td>1</td>
<td>14.9</td>
<td>26.9</td>
<td>1.81</td>
<td>29.5</td>
</tr>
<tr>
<td>Poly(VBP)</td>
<td>50</td>
<td>1</td>
<td></td>
<td></td>
<td></td>
<td>39.0</td>
</tr>
</tbody>
</table>

**NB**
1 Polymerisation time Poly(4-VP) = 18 hours, Poly(2-VP) = 18 hours, Poly(VBP) = 24 hours
   total [Monomer] = 20% w/v in DMF
2 [I] = AIBN (w/w) on monomer
3 GPC in DMF + 0.1%wt LiBr molar masses kg.mol$^{-1}$
4 MO = membrane osmometry molar masses kg.mol$^{-1}$
to the PS segments, 4-vinylpyridine was copolymerised with diphenyl-terminated PS. The conditions were analogous to the copolymerisation of macromonomers. Products after purification to remove unreacted starting materials were analysed by $^1$H nmr. No peaks attributable to PS could be found. The spectrum was exactly the same as poly(4-vinylpyridine) homopolymer. Therefore, transfer reactions were considered not to provide a significant contribution to copolymerisation.

4.4.1 Nuclear magnetic spectroscopy

For graft copolymers having a vinylpyridine type backbone, a comparison of the integration of the aromatic proton(s) on the neighbouring carbon atom ($\delta = 8.0$ ppm) to the nitrogen atom with the total integration of the aromatic protons permits calculation of the copolymer composition. For graft copolymers having a vinylbenzylpyrrolidine type backbone, the integration of the methylene bridge protons between the nitrogen and aromatic group at $\delta = 4.2$ ppm compared to the total integration of aromatic protons gives the copolymer composition.

4.4.2 Membrane Osmometry

The number average molar mass $M_n$ was determined for the graft copolymers used as stabilisers in dispersion polymerisations. Plots of $\pi/c$ vs $c$ were linear over the concentrations used. Figure 4.1 shows a typical plot for extrapolation to $c=0$. The osmotic pressure and $M_n$ are related according to the following virial expansion:

$$\frac{\pi}{c} = \frac{RT}{M_n} + Bc + Cc^2 + \ldots$$

(4.3)

where $\pi$ is the osmotic pressure, $c$ is the polymer concentration in g.1$^{-1}$, $R$ is the gas constant, $T$ is the absolute temperature and $B$ and $C$ are the second and third virial coefficients.

As $c$ approaches zero:

$$\left(\frac{\pi}{c}\right)_{c=0} = \frac{RT}{M_n}$$

- 68 -
Figure 4.1

Plot of reduced osmotic pressure against concentration for G11D and poly(4-VP)C in DMF + 0.1M LiBr at 307K.
Therefore, $M_n$ is obtained from the intercept of the above line. The second virial coefficient can be derived from the gradient of the line. In a good solvent the gradient of the line is positive. A negative slope is observed in poor solvents and a zero gradient at theta conditions.

Osmometry gives values of $M_n$ for the graft copolymers and homopolymers without the need for calibration. These values together with information on copolymer composition and macromonomer molar mass were used to calculate the number of grafts per chain and the average spacing between grafts along the backbone.

4.4.3 Gel Permeation Chromatography

GPC in DMF was used to determine molar masses and distributions in a similar manner to the analysis of polystyrene macromonomers. Aggregation of polymer molecules in solution was prevented by the addition of lithium bromide to the eluent. The column was calibrated with narrow molar mass distribution poly(ethylene oxide) standards. The molar masses determined are therefore with respect to poly(ethylene oxide). The values obtained for the number and weight average molar masses ($M_n$ and $M_w$) were not corrected for peak broadening and the polydispersity index represents a maximum value. The calibration curve for polystyrene standards in DMF does not obey the same relationship as poly(ethylene oxide); this is illustrated in figure 4.2. Determination of the true molar masses of the graft copolymers is complex involving interpolation between the two calibration curves, which will vary with copolymer composition. The polydispersity index will only give an estimate of the molar mass distribution.

4.4.4 Thermal Analysis

Table 4.11 presents data on the glass transition temperatures of the graft copolymers and other related polymers using differential scanning calorimetry and dynamic mechanical
FIGURE 4.2

CALIBRATION PLOT OF PEAK MOLAR MASS VERSUS RETENTION VOLUME FOR PEO & PS IN DMF (0.1% wt LiBr) AT 353K
### TABLE 4.11
GLASS TRANSITION TEMPERATURES
HOMOPOLYMERS AND GRAFT COPOLYMERS

<table>
<thead>
<tr>
<th>Code</th>
<th>DSC $T_g$ (K)</th>
<th>DMTA $T_g$ (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>M5</td>
<td>358</td>
<td>367</td>
</tr>
<tr>
<td>Poly(2-VP)</td>
<td>377</td>
<td>386</td>
</tr>
<tr>
<td>Poly(4-VP)A</td>
<td>422</td>
<td>428</td>
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<tr>
<td>Poly(VBP)</td>
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<td>377</td>
</tr>
<tr>
<td>G11A</td>
<td>367 &amp; 423</td>
<td>432</td>
</tr>
<tr>
<td>G11B</td>
<td>372 &amp; 419</td>
<td>429</td>
</tr>
<tr>
<td>G11C</td>
<td>370 &amp; 417</td>
<td>415</td>
</tr>
<tr>
<td>G11D</td>
<td>368-403 broad</td>
<td>358-413 broad</td>
</tr>
<tr>
<td>G12A</td>
<td></td>
<td>389</td>
</tr>
<tr>
<td>G12B</td>
<td></td>
<td>384</td>
</tr>
<tr>
<td>G12C</td>
<td></td>
<td>283</td>
</tr>
<tr>
<td>G12D</td>
<td>375</td>
<td>283</td>
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<tr>
<td>G14A</td>
<td></td>
<td>367</td>
</tr>
<tr>
<td>G14B</td>
<td></td>
<td>376</td>
</tr>
<tr>
<td>G14C</td>
<td></td>
<td>377</td>
</tr>
<tr>
<td>G14D</td>
<td></td>
<td>380</td>
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</tbody>
</table>
thermal analysis. Figure 4.3 show results from DMTA for the G11 series of graft copolymers.

4.5 MICELLAR DISPERSIONS

Micellar disperisons were characterised by TEM and SAXS. Results are presented in table 4.12.

4.5.1 Transmission Electron Microscopy

Particle size was estimated by TEM, which also gave an indication of the geometry of the particles. Figures 4.4 to 4.6 show typical electron micrographs for micelles formed in different diluents. In general, at least 40-50 individual measurements of micelle diameters were measured. The average micelle diameter as quoted is the number average \( D_n \) given by

\[
D_n = \frac{\sum N_i D_i}{\sum N_i}
\]  

(4.5)

where \( N_i \) is the number of micelles of diameter \( D_i \). An indication of the breadth of the micelle distribution is given by the ratio \( D_s/D_n \), where \( D_s \) is given by

\[
D_s = \frac{\sum N_i (D_i)^2}{\sum N_i D_i}
\]  

(4.6)

4.5.2 Small-Angle X-ray Scattering

SAXS can provide information of micelle dimensions including the radius of the core and fringe thickness. As described in section 3.9.3.4 in order to determine the core radius, the data must be desmeared. Figure 4.7 and 4.8 illustrate the effect of desmeasuring the data to pinhole optics.

(a) Core Size Determination

Guinier\textsuperscript{168,169} proposed that at the lowest angular region the radius of gyration \( R_g \) can be obtained from the plot of \( \ln(\text{desmeared Intensity}) \) vs \( 4\pi s^2/3 \). This plot is presented in...
DMTA

Head: Standard 300°C

Title: Poly (4VP)-g-PS  Date Run: Aug/23/1991
Subtitle: Pressed Film  Freq: 1
Filename: Strain: 4
Operator: M.G.Branch  Dim: 2.00, 11.568, .483

Temperature (°C)

Bending E' (MPa)

Bending tan δ

159°C = G11A  156°C = G11B  141°C = G11C  115°C = G11D
### TABLE 4.12
CHARACTERISATION OF MICELLAR DISPERSIONS

<table>
<thead>
<tr>
<th>Graft Code</th>
<th>Copolymer</th>
<th>Diluent</th>
<th>Porod's Fringe Thickness</th>
<th>TEM</th>
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<td></td>
<td></td>
<td>Rg</td>
<td>Rsp</td>
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<tr>
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<td>13.3</td>
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<td>G11D</td>
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<td>9.6</td>
<td>12.4</td>
</tr>
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</tr>
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</tr>
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(Continued)
<table>
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<th>Graft Code</th>
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<th>$R_{sp}$</th>
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<td>MD36</td>
<td>MD36</td>
<td>Ethyl Benzene</td>
<td>10.0</td>
<td>12.9</td>
<td>-ve</td>
<td>3.3  7.3</td>
</tr>
<tr>
<td>MD39</td>
<td>MD39</td>
<td>Oligostyrene</td>
<td>10.6</td>
<td>13.7</td>
<td>no dev.</td>
<td></td>
</tr>
<tr>
<td>MD40</td>
<td>MD40</td>
<td>Oligostyrene</td>
<td>4.1</td>
<td>5.3</td>
<td>+ve</td>
<td></td>
</tr>
</tbody>
</table>

NB $R_g$, $R_{sp}$ and Fringe Thickness in nm.

[micelles] = 3% by wt. on total weight.
FIGURE 4.4
TRANSMISSION ELECTRON MICROGRAPHS
OF MICELLAR DISPERSIONS IN CYCLOHEXANE

(a) MD24 Gl1B/Cyclohexane

(b) MD18 Gl1C/Cyclohexane

(c) MD20 Gl1D/Cyclohexane
FIGURE 4.5
TRANSMISSION ELECTRON MICROGRAPHS
OF MICELLAR DISPERSIONS

(a) MD13 G11B/Toluene

(b) MD17 G11C/Toluene

(c) MD16 G14C/Cyclohexane
FIGURE 4.6
TRANSMISSION ELECTRON MICROGRAPHS
OF MICELLAR DISPERSIONS IN METHANOL

(a) MD30 G12A/Methanol

(b) MD31 G12B/Methanol

(c) MD32 G12C/Methanol
FIGURE 4.7

SMEARED INTENSITY vs 2θ FOR MD13 (G11B/TOLUENE)
Figure 4.8

Desmeared Intensity vs $2\theta$ for MD13 (G11B/Toluene)
The values of $R_g$ is given by $(-\text{gradient})^{0.5}$ over the linear region at the lowest angles.

No assumption of micellar shape has been made in the determination of $R_g$, although the more asymmetrical the core shape the smaller the region where the Guinier expression is valid. If the core radius is assumed to be spherical, the micellar radius ($R_{sp}$) is defined by equation 2.23.

(b) Fringe Thickness

The fringe thickness can only be calculated when negative deviations from Porod's Law are observed. A plot of $s^3 I$ vs $s$ will at high values of $s$ have zero gradient when no deviations occur. An example of a Porod Plot with negative deviations from Porod's Law is presented in figure 4.10.

There are two models for the interfacial fringe layer used here. The first assumes the change in electron density from the core boundary to the edge of the fringe follows a linear gradient while the other uses a sigmoidal gradient. There are a number of graphical approximations for these two models. These approximations are only valid over a certain angular range. The Vonk and Empirical approximations were used as they were the only two that were valid.

(i) Vonk Approximation\textsuperscript{173}

The Vonk approximation for infinite height slit optics (i.e. smeared intensities) is given by a plot of $s^3 I$ vs $s^2$ where the interfacial fringe thickness is given by:

$$\delta = \left( \frac{-3.\text{grad.}}{2s^2.\text{int.}} \right)^{1/2}$$  \hspace{1cm} (4.7)

Figure 4.11 shows a typical Vonk plot for G11B in toluene. Only the highest angular region is plotted where the relationship is linear.
FIGURE 4.9

GUINIER PLOT OF MD13 (G11B/TOLUENE)

\[ y = 5.44 \times 10^0 - 9.21 \times 10^3 x \]

\[ r^2 = 9.97 \times 10^{-1} \]
FIGURE 4.10

POROD'S LAW PLOT OF MD13 (G11B/TOLUENE)

Region of Interest
FIGURE 4.11

$s^3 I$ vs $s^2$ (AT HIGH $2\theta$) FOR MD13 (G11B/TOLUENE)

$y = 4.11E-5 - 1.51E-1x \quad r^2 = 9.25E-1$
(ii) Empirical Approximation

The empirical approximation is given by a plot of \( \ln(s^3 I) \) vs \( s^{1.81} \) shown in figure 4.12. From this plot the standard deviation of the Gaussian function (\( \sigma \)) is given by

\[
\sigma = \left( \frac{-\text{grad.}}{38} \right)^{1/1.81} \tag{4.8}
\]

The Gaussian function describes the fringe thickness and can be related to \( \delta \) by the following relationship.

\[
\delta = 12^{0.5} \sigma \tag{4.9}
\]

4.6 DIPSERSION POLYMERISATION

Tables 4.13 to 4.16 record the results of dispersion polymerisations of the four systems studied. Sizes of particles constituted from addition polymers (e.g. PMMA, PS and P4VP) were investigated by TEM as described in section 4.5.1. PET particle sizes were analysed by using SEM. Because of the wide size distribution observed in these systems no number and size average diameters (\( D_n, D_s \)) are quoted. Figures 4.13 to 4.19 present micrographs of the four dispersion systems.

The stabiliser content was determined for a number of the dispersions and results are presented in table 4.17 & 4.18. The molar masses of the dispersed phase was also determined by GPC with THF as the eluent for PMMA and PS particles. Results are presented in table 4.19. SAXS was also performed on the particles from the dispersion polymerisations of FRD 36, 37 and 38, results are presented in table 4.20. The molar mass of the PET from dispersion D16 was determined by GPC in o-chlorophenol at 403K by ICI Wilton Materials Research Centre. The results are based on polystyrene calibration molar masses.

\[
M_n = 83,800
\]
\[ M_w = 197,000 \]
\[ M_w/M_n = 2.35 \]
FIGURE 4.12

\[ y = -5.98 \times 10^0 - 2.41 \times 10^3 x \]

\[ r^2 = 9.40 \times 10^{-1} \]

\[ \ln(s.I) \text{ vs } s \text{ FOR MD13 (G11B/TOLUENE)} \]
FIGURE 4.13
TRANSMISSION ELECTRON MICROGRAPHS OF PMMA PARTICLES
IN CYCLOHEXANE STABILISED WITH DIFFERENT GRAFT COPOLYMERS

(a) FRD1 stabilised with G12B

(b) FRD2 stabilised with G12C

(c) FRD3 stabilised with G12D
FIGURE 4.14
ELECTRON MICROGRAPHS OF PMMA PARTICLES
IN CYCLOHEXANE STABILISED WITH G11D

(a) FRD6 stabilised with 4.7% by wt. G11D

(b) FRD31 stabilised with 1.0% by wt. G11D

(i) TEM

(ii) SEM
FIGURE 4.15
ELECTRON MICROGRAPHS OF POLY(4-VP) PARTICLES IN TOLUENE STABILISED WITH DIFFERENT GRAFT COPOLYMERS

(a) FRD36 stabilised with G11B

(b) FRD37 stabilised with G11C

(c) FRD38 stabilised with G11D
FIGURE 4.16
ELECTRON MICROGRAPHS OF POLY(4-VP) PARTICLES STABILISED WITH DIFFERENT GRAFT COPOLYMERS

(a) FRD65 stabilised with G12C in toluene

(b) FRD66 stabilised with G12C in cyclohexane

(c) FRD67 poly(2-VP) stabilised with G12C in cyclohexane
FIGURE 4.17
ELECTRON MICROGRAPHS OF PS PARTICLES STABILISED WITH HOMOPOLYMERS

(a) FRD42 stabilised with poly(2-VP)

(b) FRD43 stabilised with poly(VBP)

(c) FRD46 stabilised with poly(4-VP)
FIGURE 4.18
ELECTRON MICROGRAPHS OF PS PARTICLES STABILISED WITH GRAFT COPOLYMERS

(a) FRD21 stabilised with G11A

(b) FRD22 stabilised with G11B

(c) FRD23 stabilised with G11C
FIGURE 4.19
ELECTRON MICROGRAPHS OF PET PARTICLES

(a) D16 stabilised with G14B (unwashed)

(b) D16 stabilised with G14B (washed dichloromethane)
## Table 4.13

**Dispersion Polymerisations of MMA in Cyclohexane**

<table>
<thead>
<tr>
<th>Code</th>
<th>Graft</th>
<th>[S]</th>
<th>[M]</th>
<th>[I]</th>
<th>% Conversion</th>
<th>Method</th>
<th>$D_n$</th>
<th>$D_s/D_n$</th>
<th>Comments</th>
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<td>after 1 hour</td>
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<td>.27</td>
<td>1.03</td>
<td>spherical, not smooth</td>
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</table>

(continued)
### TABLE 4.13 (continued)

**DISPERSION POLYMERISATIONS OF MMA IN CYCLOHEXANE**

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<tr>
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<th>[M]</th>
<th>[I]</th>
<th>% wt</th>
<th>Method</th>
<th>$D_n$</th>
<th>$D_s/D_n$</th>
<th>Comments</th>
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<td>.2</td>
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<td>C</td>
<td>.49</td>
<td>1.02</td>
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<td>G11D</td>
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<td>20.7</td>
<td>.33</td>
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<td>C</td>
<td>.53</td>
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<td>.95</td>
<td>1.02</td>
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<td>.1</td>
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<td>C</td>
<td>1.44</td>
<td>1.01</td>
<td>spherical, discrete</td>
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<td>-</td>
<td>A</td>
<td>.25</td>
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<td>.1</td>
<td>-</td>
<td>A</td>
<td></td>
<td></td>
<td>flocculated</td>
</tr>
</tbody>
</table>

**NB**

(a) Stabiliser [S], monomer [M] and initiator [I] concentrations based on total weight (including cyclohexane).

(b) Method

A = one shot for 2 hours.

B = seed 20% [M], [I] 100% [S] for 2 hours; feed 80% [M], [I] over ½ hour total polymerisation time = 22 hours.

C = one shot for 22 hours.

D = seed 20% [M], [I] 100% [S] for 1 hour; feed 20% [M], [I] every ¼ hour for 1½ hours; total polymerisation time = 22 hours.
### TABLE 4.14
DISPERSION POLYMERISATIONS OF 4-VP IN CYCLOHEXANE/TOLUENE

<table>
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<th>Code</th>
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<th>[S]</th>
<th>[M]</th>
<th>[I]</th>
<th>% Diluent</th>
<th>Dn (μm)</th>
<th>Dg/Dn</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
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<td>G11B</td>
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<td>.1</td>
<td>-</td>
<td>Cyclohexane</td>
<td>flocculated after 1 hour</td>
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<td>G11C</td>
<td>4.7</td>
<td>20.5</td>
<td>.1</td>
<td>-</td>
<td>Cyclohexane</td>
<td>flocculated</td>
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<td>G11D</td>
<td>4.7</td>
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<td>.1</td>
<td>-</td>
<td>Cyclohexane</td>
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<td>.1</td>
<td>94</td>
<td>Toluene</td>
<td>.22 1.01 spherical, discrete</td>
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<td>.1</td>
<td>98</td>
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### DISPERSION POLYMERISATIONS OF 2-VP IN CYCLOHEXANE

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<th>[I]</th>
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<td>95</td>
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</table>

NB

One shot polymerisation, time = 22 hours

[S], [M] and [I] based on total weight (including diluent).
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<tr>
<th>Code</th>
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<th>[M]</th>
<th>[I]</th>
<th>%</th>
<th>Method Dn</th>
<th>Dₛ/Dₙ</th>
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<td>.12 1.12 spherical, discrete</td>
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<td>C</td>
<td>.13 1.22 spherical, discrete</td>
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<td>21.1</td>
<td>.1</td>
<td>93</td>
<td>C</td>
<td>5.0 coarse, irregular</td>
</tr>
<tr>
<td>FRD28</td>
<td>G14C</td>
<td>4.7</td>
<td>20.8</td>
<td>.1</td>
<td>-</td>
<td>C</td>
<td>0.7 in groups of 10um particles</td>
</tr>
<tr>
<td>FRD42</td>
<td>P(2VP)</td>
<td>4.6</td>
<td>20.7</td>
<td>.1</td>
<td>67</td>
<td>C</td>
<td>1.8 1.00 spherical, discrete</td>
</tr>
<tr>
<td>FRD43</td>
<td>P(4VP)A</td>
<td>4.6</td>
<td>21.4</td>
<td>.1</td>
<td>85</td>
<td>C</td>
<td>.61 1.12 spherical, discrete</td>
</tr>
<tr>
<td>FRD44</td>
<td>P(VbP)</td>
<td>4.7</td>
<td>20.8</td>
<td>.1</td>
<td>84</td>
<td>C</td>
<td>.29 1.21 spherical, bridging</td>
</tr>
<tr>
<td>FRD45</td>
<td>G11A</td>
<td>4.6</td>
<td>20.7</td>
<td>.1</td>
<td>59</td>
<td>B</td>
<td>.053 1.46 spherical, discrete</td>
</tr>
<tr>
<td>FRD46</td>
<td>P(4VP)A</td>
<td>4.6</td>
<td>20.7</td>
<td>.1</td>
<td>56</td>
<td>B</td>
<td>.67 1.01 spherical, discrete</td>
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<tr>
<td>FRD47</td>
<td>G11B</td>
<td>4.6</td>
<td>20.7</td>
<td>.1</td>
<td>60</td>
<td>B</td>
<td>.038 1.17 spherical, discrete</td>
</tr>
<tr>
<td>FRD48</td>
<td>G11C</td>
<td>4.6</td>
<td>20.9</td>
<td>.1</td>
<td>63</td>
<td>B</td>
<td>.049 1.03 spherical, bridging</td>
</tr>
<tr>
<td>FRD49</td>
<td>G11A</td>
<td>4.7</td>
<td>20.7</td>
<td>.1</td>
<td>76</td>
<td>D</td>
<td>.042 1.51 spherical, discrete</td>
</tr>
</tbody>
</table>

(continued)
### TABLE 4.15 (continued)

**DISPERSION POLYMERISATIONS OF STYRENE IN METHANOL**

<table>
<thead>
<tr>
<th>Code</th>
<th>Stabiliser</th>
<th>[S]</th>
<th>[M]</th>
<th>[I]</th>
<th>% Conversion</th>
<th>Method</th>
<th>(D_n) (\mu m)</th>
<th>(D_s/D_n)</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>FRD50</td>
<td>P(4VP)A</td>
<td>4.7</td>
<td>20.7</td>
<td>0.1</td>
<td>76</td>
<td>D</td>
<td>0.82</td>
<td>1.01</td>
<td>spherical, discrete</td>
</tr>
<tr>
<td>FRD51</td>
<td>G11B</td>
<td>4.6</td>
<td>20.6</td>
<td>0.1</td>
<td>-</td>
<td>D</td>
<td>0.036</td>
<td>1.20</td>
<td>spherical, a little bridging</td>
</tr>
<tr>
<td>FRD52</td>
<td>G11C</td>
<td>4.8</td>
<td>20.7</td>
<td>0.1</td>
<td>-</td>
<td>D</td>
<td>0.046</td>
<td>1.08</td>
<td>spherical, bridging</td>
</tr>
<tr>
<td>FRD55</td>
<td>P(4VP)A</td>
<td>2.9</td>
<td>21.3</td>
<td>0.1</td>
<td>79</td>
<td>C</td>
<td>0.95</td>
<td>1.02</td>
<td>spherical, discrete</td>
</tr>
<tr>
<td>FRD56</td>
<td>P(4VP)A</td>
<td>1.2</td>
<td>21.5</td>
<td>0.1</td>
<td>90</td>
<td>C</td>
<td>1.29</td>
<td>1.01</td>
<td>spherical, discrete</td>
</tr>
<tr>
<td>FRD59</td>
<td>G11A</td>
<td>2.3</td>
<td>21.3</td>
<td>0.1</td>
<td>97</td>
<td>C</td>
<td>0.096</td>
<td>1.35</td>
<td>spherical, discrete</td>
</tr>
<tr>
<td>FRD60</td>
<td>G11A</td>
<td>1.0</td>
<td>21.4</td>
<td>0.1</td>
<td>81</td>
<td>C</td>
<td>0.15</td>
<td>1.28</td>
<td>spherical, discrete</td>
</tr>
<tr>
<td>FRD62</td>
<td>G11B</td>
<td>1.1</td>
<td>21.7</td>
<td>0.1</td>
<td>77</td>
<td>C</td>
<td>0.14</td>
<td>1.03</td>
<td>occasional odd shape</td>
</tr>
<tr>
<td>FRD63</td>
<td>P(4VP)B</td>
<td>4.6</td>
<td>20.7</td>
<td>0.1</td>
<td>79</td>
<td>C</td>
<td>0.83</td>
<td>1.02</td>
<td>spherical, discrete</td>
</tr>
<tr>
<td>FRD64</td>
<td>P(4VP)C</td>
<td>4.6</td>
<td>20.5</td>
<td>0.1</td>
<td>84</td>
<td>C</td>
<td>0.77</td>
<td>1.08</td>
<td>spherical, discrete</td>
</tr>
</tbody>
</table>

**NB**
(a) Stabiliser, monomer and initiator concentrations based on total weight (including methanol).
(b) Method
- **A** = one shot for 2 hours.
- **B** = seed 20% [M], [I] 100% [S] for 2 hours; feed 80% [M], [I] over \(\frac{1}{2}\) hour total polymerisation time = 22 hours.
- **C** = one shot for 22 hours.
- **D** = seed 20% [M], [I] 100% [S] for 1 hour; feed 20% [M], [I] every \(\frac{1}{2}\) hour for 1\(\frac{1}{2}\) hours; total polymerisation time = 22 hours.
<table>
<thead>
<tr>
<th>Code</th>
<th>Copolymer</th>
<th>Graft %</th>
<th>BHET</th>
<th>TIB90</th>
<th>[Cat]</th>
<th>size range</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>D1</td>
<td>G11A</td>
<td>3.0</td>
<td>14.5</td>
<td>223.4</td>
<td>14.1</td>
<td>flocculated</td>
<td></td>
</tr>
<tr>
<td>D2</td>
<td>G11B</td>
<td>3.1</td>
<td>14.3</td>
<td>220.9</td>
<td>14.2</td>
<td>flocculated</td>
<td></td>
</tr>
<tr>
<td>D3</td>
<td>G11B</td>
<td>2.9</td>
<td>15.1</td>
<td>221.2</td>
<td>13.7</td>
<td>flocculated</td>
<td></td>
</tr>
<tr>
<td>D4</td>
<td>G11C</td>
<td>3.0</td>
<td>14.0</td>
<td>211.9</td>
<td>15.3</td>
<td>flocculated</td>
<td></td>
</tr>
<tr>
<td>D5</td>
<td>G11D</td>
<td>2.8</td>
<td>15.2</td>
<td>221.3</td>
<td>15.2</td>
<td>flocculated</td>
<td></td>
</tr>
<tr>
<td>D6</td>
<td>G12A</td>
<td>2.8</td>
<td>14.9</td>
<td>221.4</td>
<td>14.3</td>
<td>flocculated</td>
<td></td>
</tr>
<tr>
<td>D7</td>
<td>G12B</td>
<td>2.8</td>
<td>14.7</td>
<td>220.5</td>
<td>15.9</td>
<td>flocculated</td>
<td></td>
</tr>
<tr>
<td>D8</td>
<td>G12C</td>
<td>3.0</td>
<td>14.0</td>
<td>221.9</td>
<td>15.6</td>
<td>flocculated</td>
<td></td>
</tr>
<tr>
<td>D9</td>
<td>G12D</td>
<td>3.0</td>
<td>14.2</td>
<td>221.7</td>
<td>14.1</td>
<td>flocculated</td>
<td></td>
</tr>
<tr>
<td>D10</td>
<td>G14A</td>
<td>2.9</td>
<td>14.3</td>
<td>220.2</td>
<td>15.7</td>
<td>1200</td>
<td>approx. spherical, smooth</td>
</tr>
<tr>
<td>D11</td>
<td>G14B</td>
<td>3.0</td>
<td>14.4</td>
<td>224.3</td>
<td>14.9</td>
<td>1000-20</td>
<td>spherical, smooth</td>
</tr>
<tr>
<td>D12</td>
<td>G14C</td>
<td>2.8</td>
<td>14.4</td>
<td>222.2</td>
<td>14.7</td>
<td>flocculated</td>
<td></td>
</tr>
<tr>
<td>D13</td>
<td>G14D</td>
<td>3.0</td>
<td>14.5</td>
<td>224.9</td>
<td>14.4</td>
<td>flocculated</td>
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</tr>
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<td>D14</td>
<td>G14C</td>
<td>3.0</td>
<td>14.3</td>
<td>221.4</td>
<td>14.3</td>
<td>flocculated</td>
<td></td>
</tr>
<tr>
<td>D15</td>
<td>G14B</td>
<td>1.0</td>
<td>14.2</td>
<td>222.4</td>
<td>14.8</td>
<td>flocculated</td>
<td></td>
</tr>
<tr>
<td>D16</td>
<td>G14B</td>
<td>4.8</td>
<td>14.5</td>
<td>224.9</td>
<td>15.5</td>
<td>110-&lt;5</td>
<td>smooth, spherical</td>
</tr>
</tbody>
</table>

NB
(a) [S] = % wt on BHET (not on total weight including diluent)
(b) [Cat] = catalyst Manganese II acetate tetrahydrate
(c) TIB90 = tetraisobutane 90 BHET = bishydroxyethylterephthalate.
### TABLE 4.17
DETERMINATION OF COPOLYMER CONTENT IN PMMA DISPERSIONS

<table>
<thead>
<tr>
<th>Code</th>
<th>Graft</th>
<th>Copolymer</th>
<th>Dn</th>
<th>Copolymer Content (%w/w)</th>
</tr>
</thead>
<tbody>
<tr>
<td>FRD1</td>
<td>G12B</td>
<td>.19</td>
<td></td>
<td>17.3</td>
</tr>
<tr>
<td>FRD2</td>
<td>G12C</td>
<td>.32</td>
<td></td>
<td>11.2</td>
</tr>
<tr>
<td>FRD3</td>
<td>G12C</td>
<td>.49</td>
<td></td>
<td>7.55</td>
</tr>
<tr>
<td>FRD6</td>
<td>G11D</td>
<td>.43</td>
<td></td>
<td>6.75</td>
</tr>
<tr>
<td>FRD11</td>
<td>G12B</td>
<td>.20</td>
<td></td>
<td>15.9</td>
</tr>
<tr>
<td>FRD12</td>
<td>G12C</td>
<td>.27</td>
<td></td>
<td>11.1</td>
</tr>
<tr>
<td>FRD13</td>
<td>G12D</td>
<td>.495</td>
<td></td>
<td>4.77</td>
</tr>
<tr>
<td>FRD14</td>
<td>G11D</td>
<td>.54</td>
<td></td>
<td>6.92</td>
</tr>
<tr>
<td>FRD17</td>
<td>G12B</td>
<td>.21</td>
<td></td>
<td>13.9</td>
</tr>
<tr>
<td>FRD18</td>
<td>G12C</td>
<td>.32</td>
<td></td>
<td>8.4</td>
</tr>
<tr>
<td>FRD30</td>
<td>G11D</td>
<td>.59</td>
<td></td>
<td>5.57</td>
</tr>
<tr>
<td>FRD31</td>
<td>G11D</td>
<td>.92</td>
<td></td>
<td>4.36</td>
</tr>
<tr>
<td>FRD41</td>
<td>G11D</td>
<td>.63</td>
<td></td>
<td>8.10</td>
</tr>
<tr>
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<td>G12D</td>
<td>.95</td>
<td></td>
<td>3.40</td>
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<tr>
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<td>G12D</td>
<td>1.44</td>
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### TABLE 4.18
DETERMINATION OF STABILISER CONTENT IN PS DISPERSIONS

<table>
<thead>
<tr>
<th>Code</th>
<th>Stabiliser</th>
<th>Dn</th>
<th>Content (%w/w)</th>
</tr>
</thead>
<tbody>
<tr>
<td>FRD43</td>
<td>P(4VP)A</td>
<td>.61</td>
<td>.24</td>
</tr>
<tr>
<td>FRD46</td>
<td>P(4VP)A</td>
<td>.67</td>
<td>.19</td>
</tr>
<tr>
<td>FRD50</td>
<td>P(4VP)A</td>
<td>.815</td>
<td>.087</td>
</tr>
<tr>
<td>FRD55</td>
<td>P(4VP)A</td>
<td>.95</td>
<td>.15</td>
</tr>
<tr>
<td>FRD56</td>
<td>P(4VP)A</td>
<td>1.29</td>
<td>.038</td>
</tr>
<tr>
<td>FRD63</td>
<td>P(4VP)B</td>
<td>.83</td>
<td>.043</td>
</tr>
<tr>
<td>FRD64</td>
<td>P(4VP)C</td>
<td>.77</td>
<td>.063</td>
</tr>
</tbody>
</table>

**NB**

Copolymer content of PMMA particles determined by UV spectroscopy.

Stabiliser content of PS particles determined by $^1$H nmr.
## TABLE 4.19

GPC DATA FOR PMMA AND PS DISPERSIONS

<table>
<thead>
<tr>
<th>Code</th>
<th>Particle</th>
<th>Stabiliser</th>
<th>( D_n )</th>
<th>GPC kg.mol(^{-1} )</th>
<th>( M_n )</th>
<th>( M_w )</th>
<th>Mmd</th>
</tr>
</thead>
<tbody>
<tr>
<td>FRD3</td>
<td>PMMA</td>
<td>G12D</td>
<td>.49</td>
<td>210.9</td>
<td>423.3</td>
<td>2.01</td>
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</tr>
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<td>PMMA</td>
<td>G11D</td>
<td>.43</td>
<td>254.6</td>
<td>546.2</td>
<td>2.15</td>
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</tr>
<tr>
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<td>PMMA</td>
<td>G12D</td>
<td>.495</td>
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<td>395.4</td>
<td>3.92</td>
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</tr>
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<td>PMMA</td>
<td>G11D</td>
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<td>228.8</td>
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<tr>
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<td>PMMA</td>
<td>G11D</td>
<td>.59</td>
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<td>453.8</td>
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<td>PMMA</td>
<td>G11D</td>
<td>.92</td>
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<td>393.1</td>
<td>3.64</td>
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</tr>
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<td>PMMA</td>
<td>G11D</td>
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<td>G12D</td>
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<td>PS</td>
<td>P(4VP)A</td>
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<td>495.5</td>
<td>3.75</td>
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</tr>
<tr>
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<td>PS</td>
<td>P(4VP)A</td>
<td>.95</td>
<td>119.6</td>
<td>539.9</td>
<td>4.51</td>
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</tr>
<tr>
<td>FRD56</td>
<td>PS</td>
<td>P(4VP)A</td>
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<td>107.5</td>
<td>495.2</td>
<td>4.61</td>
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</tr>
<tr>
<td>FRD59</td>
<td>PS</td>
<td>G11A</td>
<td>.096</td>
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<tr>
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<td>PS</td>
<td>P(4VP)B</td>
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</tr>
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<td>FRD64</td>
<td>PS</td>
<td>P(4VP)C</td>
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<td>139.4</td>
<td>548.5</td>
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</tbody>
</table>

NB

GPC performed with THF as eluent with PL mixed gel 10u 60 cm column.
<table>
<thead>
<tr>
<th>Graft Code Copolymer</th>
<th>Diluent</th>
<th>Porod's Fringe Thickness</th>
<th>TEM</th>
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</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>R_g</td>
<td>R_sp</td>
</tr>
<tr>
<td>FRD36 G11B Toluene</td>
<td>29.1</td>
<td>37.5</td>
<td>-ve</td>
</tr>
<tr>
<td>FRD37 G11C Toluene</td>
<td>27.2</td>
<td>35.0</td>
<td>-ve</td>
</tr>
<tr>
<td>FRD38 G11D Toluene</td>
<td>31.8</td>
<td>41.0</td>
<td>-ve</td>
</tr>
</tbody>
</table>

NB R_g, R_sp and Fringe Thickness in nm.
5 DISCUSSION

5.1 PREPARATION OF THE MACROMONOMERS

The errors involved in the determination of molar masses by GPC are about 5%. A slightly wider than Poisson distribution is observed which may be explained in terms of imperfect mixing of the contents of the polymerisation reactor as polymer concentrations of 30% were typically used. The addition of THF to the polymerisation medium ensured rapid initiation of the styrene by breaking up the associated sec-butyl lithium in hydrocarbon media\textsuperscript{82,85}. Rapid initiation is desirable to ensure a narrow molar mass distribution. The peaks in the nmr used to determine both $M_n$ and the functionality are endgroups in the macromonomer. It is therefore predicted that the errors involved will become progressively larger with increasing molar mass. For polystyrene of $M_n=3.2$ kg.mol\textsuperscript{-1} these errors may be as much as 10%. It can be concluded that the macromonomers maybe considered to be quantitatively monofunctional from the data presented in this work. The molar masses obtained were usually within 10% of the molar mass predicted by equation 2.8. Therefore, rapid quantitative initiation is observed. The molar mass results derived from $^1$H nmr were used in further calculations for the graft copolymers.

Diphenylethylene was used to modify the nucleophilicity of the polystyryl carbanion prior to the addition of vinylbenzyl chloride because attack of the double bond was found to take place in competition with substitution at the chloromethylene group. This has also been observed by other workers\textsuperscript{97,98}, although Asami\textsuperscript{14} noted that under certain conditions, diphenylethylene is not required.

The data presented in table 4.1 compares favorably with the literature values presented in table 5.1

5.2 PREPARATION OF N-(VINYLBENZYL)PYRROLIDONE

VBP was easily produced in high yields. The reaction was found to require the addition of triethylamine, otherwise no
<table>
<thead>
<tr>
<th>Mechanism</th>
<th>Polymer</th>
<th>End-Group Functionality</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>polysiloxane methacrylate</td>
<td>.96-1.00</td>
<td>111</td>
</tr>
<tr>
<td>A</td>
<td>polysiloxane styrene</td>
<td>.84-1.07</td>
<td>112</td>
</tr>
<tr>
<td>A</td>
<td>PEO methacrylate/styrene</td>
<td>.85-1.00</td>
<td>107,108</td>
</tr>
<tr>
<td>A</td>
<td>poly(butylacrylate) styrene</td>
<td>1.12</td>
<td>109</td>
</tr>
<tr>
<td>A</td>
<td>poly(2-VP) styrene</td>
<td>&gt;.96</td>
<td>105,106</td>
</tr>
<tr>
<td>A</td>
<td>PMMA styrene methacrylate/styrene</td>
<td>&gt;.85</td>
<td>107,10102</td>
</tr>
<tr>
<td>A</td>
<td>PS styrene</td>
<td>.86-.96</td>
<td>14</td>
</tr>
<tr>
<td>F</td>
<td>poly(vinylpyrrolidone) styrene</td>
<td>&gt;.95</td>
<td>128</td>
</tr>
<tr>
<td>F</td>
<td>PS allyl</td>
<td>1.0-1.2</td>
<td>184</td>
</tr>
<tr>
<td>F</td>
<td>PS styrene</td>
<td>.83</td>
<td>183</td>
</tr>
<tr>
<td>C</td>
<td>poly(tetrahydrofuran) methacrylate/styrene</td>
<td>.8-.10</td>
<td>115</td>
</tr>
<tr>
<td>C</td>
<td>poly(tetrahydrofuran) styrene</td>
<td>.9-.11</td>
<td>118</td>
</tr>
<tr>
<td>C</td>
<td>poly(isobutylene) styrene</td>
<td>.9-.11</td>
<td>119</td>
</tr>
<tr>
<td>GT</td>
<td>PMMA styrene</td>
<td>.83</td>
<td>122</td>
</tr>
</tbody>
</table>

A = anionic polymerisation  F = free-radical polymerisation
C = cationic polymerisation  GT = group-transfer polymerisation
product was obtained. It is thought that triethylamine hydrochloride which precipitates from the reaction medium pushes the equilibrium reaction to completion.

5.3 STATISTICAL COPOLYMERS

Monomer reactivity ratios were determined by Fineman-Ross and Kelen-Tudos linear least squares methods using the copolymer compositions from table 4.5 and 4.6. These are presented in table 5.2. Comparison of the values obtained here for vinyl pyridine/styrene copolymerisations with data from the literature show some differences. These may be due to a number of factors. In some cases, the previous work determined the copolymer compositions by nitrogen analysis. This assumes the complete combustion of the copolymer which may not occur leading to imprecise copolymer compositions. Benzene has been used as a solvent system for copolymerisations for 4-vinylpyridine in previous work\textsuperscript{185}, even though poly(4-vinylpyridine) is a non-solvent in benzene. In the present work DMF has been used thus ensuring that the polymerisation system is homogeneous. Differences may also be attributable to solvent effects which can occur with copolymerisations using polar monomers. Smets et al\textsuperscript{186} performed copolymerisations of other styryl substituted pyrrolidones and piperidones observing similar reactivity ratios to the present system.

5.4 GRAFT COPOLYMERS

GPC in DMF of the graft copolymers showed the presence of aggregation when no lithium bromide was added to the eluent. Polydispersities varied from 1.80 to 2.10 for the graft copolymers. Homopolymers showed similar molar mass distributions. These polydispersities are typical of conventional mechanisms for free-radical polymerisation. It is assumed that the polydispersity of the graft copolymer is not altered by the PS grafts interacting with the gel on the column. The molar masses determined by GPC show that increasing amounts of PS in the graft copolymer increase the amount of
<table>
<thead>
<tr>
<th>Code</th>
<th>Monomer</th>
<th>Fineman-Ross</th>
<th>Kelen-Tudos</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$r_1$</td>
<td>$r_2$</td>
</tr>
<tr>
<td>C9</td>
<td>2-VP/Sty</td>
<td>.76</td>
<td>.279</td>
</tr>
<tr>
<td>C10</td>
<td>4-VP/Sty</td>
<td>1.0</td>
<td>.34</td>
</tr>
<tr>
<td>C16</td>
<td>VBP/Sty</td>
<td>.77</td>
<td>.89</td>
</tr>
</tbody>
</table>

**LITERATURE VALUES FOR THE MONOMER REACTIVITY RATIOS**

<table>
<thead>
<tr>
<th>Monomer</th>
<th>$r_1$</th>
<th>$r_2$</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-VP/Sty</td>
<td>1.13</td>
<td>.55</td>
<td>187</td>
</tr>
<tr>
<td></td>
<td>1.81</td>
<td>.55</td>
<td>188</td>
</tr>
<tr>
<td></td>
<td>.90</td>
<td>.56</td>
<td>189</td>
</tr>
<tr>
<td>4-VP/Sty</td>
<td>.70</td>
<td>.54</td>
<td>189</td>
</tr>
<tr>
<td></td>
<td>.75</td>
<td>.57</td>
<td>185</td>
</tr>
<tr>
<td>O(\equiv)/C(\equiv)=CH(_2)=CH(_2)/Sty</td>
<td>.60</td>
<td>.84</td>
<td>186</td>
</tr>
<tr>
<td>O(\equiv)/C(\equiv)(_2)=CH(_2)=CH(_2)/Sty</td>
<td>.78</td>
<td>.94</td>
<td>186</td>
</tr>
<tr>
<td>O(\equiv)/C(\equiv)(_2)=CH(_2)=CH(_2)/Sty</td>
<td>.75</td>
<td>.90</td>
<td>186</td>
</tr>
</tbody>
</table>
interaction with the gel thereby reducing the apparent molar mass. Membrane osmometry provides a reliable method of determining $M_n$ values for both homopolymers and graft copolymers, as the technique relies on measuring the number of solute molecules via osmotic pressure. GPC operates on the steric exclusion principle, separating molecules according to their size in solution and not molar mass. Graft copolymers differ from conventional linear polymer molecules used to calibrate GPC by having a branched structure which will have a lower hydrodynamic volume than an equivalent linear polymer of the same degree of polymerisation. Molar masses of graft copolymers obtained from a linear polymer calibration may be expected to be lower than true values. It is believed that at low molar masses and low degrees of branching the effect is minimal. GPC calibration was performed using poly(ethylene oxide) standards and therefore all molar masses are with respect to PEO. Dawkins has shown that the same molar mass calibration curve is obtained for polymers with similar unperturbed dimensions per unit mass. If the unperturbed mean square end-to-end distance $<r_o^2>$ is taken as the universal calibration parameter, the molar mass calibrations at a given elution volume are given by

$$\log M_x - \log M_{\text{PEO}} = \log \left( \frac{<r_o^2>}{M} \right)_{\text{PEO}} \left( \frac{M}{<r_o^2>_{\text{PEO}}} \right) x$$

(5.1)

where $<r_o^2>/M$ are the unperturbed dimensions per unit mass, $M_x$ is the molar mass of the polymer required, and $M_{\text{PEO}}$ is the molar mass of a linear poly(ethylene oxide) standard. Table 5.3 quotes the values of $(<r_o>/M)^{0.5}$ for various polymers. It can be seen that PS, poly(4-vinylpyridine) and poly(2-vinylpyridine) have similar values. Poly(N-(vinylbenzyl)pyrrolidone) being a novel monomer is not documented but it is thought that $(<r_o>/M)^{0.5}$ will be similar to poly(vinylbiphenyl). Table 5.4 presents corrected molar
<table>
<thead>
<tr>
<th>Polymer</th>
<th>$\langle r^2_0 \rangle/M^{1/2} \times 10^4$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>polystyrene</td>
<td>670</td>
</tr>
<tr>
<td>poly(2-vinylpyridine)</td>
<td>660</td>
</tr>
<tr>
<td>poly(4-vinylpyridine)</td>
<td>710</td>
</tr>
<tr>
<td>poly(ethylene oxide)</td>
<td>840</td>
</tr>
<tr>
<td>poly(vinylpyrrolidone)</td>
<td>660</td>
</tr>
<tr>
<td>poly(p-vinylbiphenyl)</td>
<td>605</td>
</tr>
<tr>
<td>Polymer</td>
<td>GPC $M_n$</td>
</tr>
<tr>
<td>--------------------</td>
<td>-----------</td>
</tr>
<tr>
<td>Poly(4-VP)A</td>
<td>16.1</td>
</tr>
<tr>
<td>Poly(2-VP)</td>
<td>14.9</td>
</tr>
<tr>
<td>G11A</td>
<td>15.9</td>
</tr>
<tr>
<td>G11B</td>
<td>12.2</td>
</tr>
<tr>
<td>G11C</td>
<td>11.4</td>
</tr>
<tr>
<td>G11D</td>
<td>10.7</td>
</tr>
<tr>
<td>G12A</td>
<td>10.9</td>
</tr>
<tr>
<td>G12B</td>
<td>8.0</td>
</tr>
<tr>
<td>G12C</td>
<td>7.6</td>
</tr>
<tr>
<td>G12D</td>
<td>6.2</td>
</tr>
</tbody>
</table>

NB
MO = membrane osmometry
Molar masses in kg.mol$^{-1}$
masses for some of the polymers analysed by GPC and compared to the values from membrane osmometry. Corrected values by GPC are still lower than values obtained by membrane osmometry. Therefore, an additional separation mechanism is taking place. Mencer and Grubisic-Gallo\textsuperscript{182} have reported on GPC separations using styragel columns in DMF and THF for PS and poly(2-VP), the separation mechanism was found to be complex in all cases except for PS in THF and concluded that the universal calibration could not be used for systems in which steric exclusion was not the only separation mechanism.

Membrane osmometry is an absolute method of determining molar mass, requiring no calibration. As it is a colligative property technique (i.e. measures number of solute molecules), aggregation effects in solution are to be avoided. It was observed that higher than expected molar masses were obtained when no lithium bromide was added to the solvent, indicating that aggregation was occurring\textsuperscript{193}. Complexation of the lithium bromide with the polymer molecules in solution prevents aggregate formation. Complexation of the lithium bromide can give rise to a concentration difference across the membrane, giving false lower than expected osmotic pressures. A large molar excess of lithium bromide compared to solute molecules is used in order to ensure the concentration difference is minimal\textsuperscript{193}.

Molar masses determined for graft copolymers and homopolymers were comparable. The molar masses obtained are due to the concentrations of total monomer and initiator used. Previous workers have attributed low molar masses to chain transfer to the macromonomer chain\textsuperscript{147,148}, low macromonomer mobility\textsuperscript{147} and lack of access to the terminal unsaturation\textsuperscript{116,147}. This is thought to be unlikely in the present work because no significant variation of graft copolymer molar mass with feed composition was observed. It is noted that the total monomer concentration was kept low in order to prevent any of the effects observed previously. $M_n$ values determined by membrane
osmometry were used in further calculations of the structure of the graft copolymers.

Thermal analysis of the graft copolymers (see table 4.11) especially the G11 series shows two glass transition temperatures. The glass transition temperature of poly(4-vinylpyridine) is reduced with increasing graft content. For G11D (the highest graft content) no glass transition temperature for poly(4-VP) is observed using DMTA. The results indicate that poly(4-vinylpyridine) is not compatible with PS, and suggest that the bulk morphology consists of domains of one component in a matrix of the other. It is thought that at low weight fractions of PS in the graft copolymer, the domains will consist of PS in a matrix of poly(4-vinylpyridine). At higher than 50% weight of PS (i.e. G11D) in the copolymer, the domains may be poly(4-vinylpyridine) in a matrix of PS. At the highest graft content (G11D) the domains of poly(4-VP) are too small to be seen by thermal analysis. The predicted minimum domain size observable by thermal methods is 15nm. Since the graft copolymers were purified by precipitation in petroleum ether 40-60; the bulk morphology may be similar to micellar behaviour in cyclohexane and toluene (see section 5.5). The micelle core diameter for G11D in cyclohexane and toluene was 10-11nm, this is smaller than the minimum domain size detectable by thermal methods.

5.4.1 Control of the Graft Copolymer Architecture

The physical and chemical properties of graft copolymers depend not only on the chemical nature of the various segments but also on their chain architecture. A schematic representation of a graft copolymer is illustrated in figure 5.1. Data for the graft copolymers used as steric stabilisers in dispersion polymerisations are shown in table 5.5. A number of important features of the graft copolymer architecture are listed below.
FIGURE 5.1
SCHEMATIC REPRESENTATION OF A GRAFT COPOLYMER

 backups arising from styrene comonomer
 grafts arising from macromonomer
 branching sites arising from macromonomer end-group
**TABLE 5.5**

**GRAFT COPOLYMERS FOR USE IN MICELLAR DISPERSIONS**
**AND AS STABILISERS IN DISPERSION POLYMERISATIONS**

<table>
<thead>
<tr>
<th>Feed Copolymer</th>
<th>MO</th>
<th>wt. fraction</th>
<th>Mac.</th>
<th>ASB</th>
<th>$M_n$</th>
<th>$M_n$(backbone)</th>
<th>$N_g$</th>
<th>$M_n$(segment)</th>
</tr>
</thead>
<tbody>
<tr>
<td>G11A 4-VP</td>
<td></td>
<td>.26</td>
<td>.16</td>
<td>5.2:1</td>
<td>36.9</td>
<td>31.0</td>
<td>1.65</td>
<td>11.7</td>
</tr>
<tr>
<td>G11B 4-VP</td>
<td></td>
<td>.50</td>
<td>.36</td>
<td>1.8:1</td>
<td>41.4</td>
<td>26.7</td>
<td>4.1</td>
<td>5.3</td>
</tr>
<tr>
<td>G11C 4-VP</td>
<td></td>
<td>.62</td>
<td>.46</td>
<td>1.2:1</td>
<td>37.0</td>
<td>20.0</td>
<td>4.7</td>
<td>3.5</td>
</tr>
<tr>
<td>G11D 4-VP</td>
<td></td>
<td>.75</td>
<td>.64</td>
<td>.45:1</td>
<td>41.9</td>
<td>15.2</td>
<td>8.4</td>
<td>1.6</td>
</tr>
<tr>
<td>G12A 2-VP</td>
<td></td>
<td>.25</td>
<td>.22</td>
<td>3.6:1</td>
<td>26.0</td>
<td>20.3</td>
<td>1.8</td>
<td>7.2</td>
</tr>
<tr>
<td>G12B 2-VP</td>
<td></td>
<td>.50</td>
<td>.36</td>
<td>1.7:1</td>
<td>27.2</td>
<td>17.3</td>
<td>3.1</td>
<td>4.2</td>
</tr>
<tr>
<td>G12C 2-VP</td>
<td></td>
<td>.63</td>
<td>.52</td>
<td>.88:1</td>
<td>31.0</td>
<td>14.8</td>
<td>5.1</td>
<td>2.5</td>
</tr>
<tr>
<td>G12D 2-VP</td>
<td></td>
<td>.74</td>
<td>.66</td>
<td>.50:1</td>
<td>29.5</td>
<td>10.0</td>
<td>6.1</td>
<td>1.4</td>
</tr>
<tr>
<td>G14A VBP</td>
<td></td>
<td>.20</td>
<td>.17</td>
<td>5.5:1</td>
<td>39.0</td>
<td>32.5</td>
<td>2.1</td>
<td>10.5</td>
</tr>
<tr>
<td>G14B VBP</td>
<td></td>
<td>.43</td>
<td>.36</td>
<td>1.8:1</td>
<td>39.0</td>
<td>25.1</td>
<td>4.5</td>
<td>4.6</td>
</tr>
<tr>
<td>G14C VBP</td>
<td></td>
<td>.60</td>
<td>.56</td>
<td>.77:1</td>
<td>39.0</td>
<td>15.5</td>
<td>7.6</td>
<td>1.8</td>
</tr>
<tr>
<td>G14D VBP</td>
<td></td>
<td>.80</td>
<td>.78</td>
<td>.28:1</td>
<td>39.3</td>
<td>8.7</td>
<td>9.8</td>
<td>0.8</td>
</tr>
</tbody>
</table>

**NB**

Molar Masses kg.mol$^{-1}$

MO=Membrane osmometry  ASB=Anchor to soluble balance  $N_g$=number of grafts per chain  

$M_n$(segment)=average molar mass of backbone between grafts (see equation 5.2)
(i) The ratio of backbone/grafts.

This is the anchor to soluble balance (ASB) as defined in section 2.2.3 for use of graft copolymers as stabilisers for polymer particles in non-aqueous media. Altering the feed composition changes the copolymer composition as can be seen in figure 5.2. Increasing the macromonomer content in the feed increases the graft content in the resulting copolymer. This is accompanied by a decrease in backbone content, since the total monomer feed concentration was kept constant. The graft content in the copolymer is always lower than the feed composition; the implications of this will be discussed in section 5.4.3.

(ii) The average number of grafts per molecule (N_g).

The variation of N_g with the comonomer feed composition is illustrated in figure 5.3. The average number of grafts per chain is low (<10) due to the low overall molar mass of the graft copolymer. N_g is readily controlled by altering the comonomer feed composition. For a given graft chain length, the number of grafts is proportional to the weight fraction of macromonomer in the feed. Generally, there is a slight increase in N_g produced as the conversion increases. These changes are due to the drift in feed composition as the copolymerisation proceeds. However, the composition drift is relatively small up to 50%, so the number of grafts per chain is not altered significantly. Conversion dependent chemical heterogeneity is low for these copolymerisations; this agrees with the predictions of Stejskal and Kratochvil that heterogeneity is only significant at high conversions. If the relative molar concentrations of the macromonomer and comonomer are considered, there is very little change even if one component is consumed far quicker in the copolymerisation than the other. In conventional copolymerisations with two low molar mass monomers, relative molar concentrations drift at lower conversions.
FIGURE 5.2

DEPENDENCE OF COPOLYMER COMPOSITION ON MACROMONOMER FEED RATIO (G11 SERIES)
FIGURE 5.3

DEPENDENCE OF NUMBER OF GRAFTS PER CHAIN ON MACROMONOMER FEED RATIO

- Poly(4-VP)-graft-PS
- Poly(2-VP)-graft-PS
Copolymers have a distribution of composition by analogy with molar mass distribution. Statistical copolymers will possess a distribution of compositions as suggested by Stockmayer. Graft copolymers likewise, will be similarly affected. It is predicted that the statistical chemical heterogeneity is substantially larger and more asymmetrical than that of conventional statistical copolymers with similar molar mass and average composition. Stejskal et al. and De Simone et al. have fractionated graft copolymers to determine the copolymer composition distribution. Both groups found that there was a wide range of compositions, agreeing with the theoretical predictions. In the present work, the graft copolymers will have similar composition distributions. It is predicted that at low \( N_g \) some homopolymer backbone will be produced. Therefore, graft copolymers with the lowest grafts per chain were further purified by removing any homopolymer backbone present as described in section 3.6. It is not possible to remove all the homopolymer as the graft copolymer micellises forming a core of homopolymer and backbone. The possibility of polymacromonomer was considered to be insignificant because of the low molar concentrations of macromonomer used in copolymerisations.

(iii) Molar masses.

The molar masses of the backbone and grafts assume that the branching site \( X \) in figure 5.1 is part of the graft. This is not strictly correct, but the errors arising from this assumption are small. Strictly, the backbone is a statistical copolymer of comonomer and styryl chain ends (from the macromonomer) with 90+ mole% comonomer. The molar masses of the grafts can be controlled easily by altering the macromonomer molar mass before copolymerisation. The overall graft copolymer molar mass can be controlled by altering the initiator concentration. The feed composition, macromonomer molar mass and initiator concentration control the molar mass of the backbone. If only the feed composition is varied, then there is
a relationship between the backbone molar mass and the concentration of macromonomer in the feed (see figure 5.4). In addition to the backbone molar mass it is possible to determine the average distance between grafts ($M_n(\text{segment})$), this is an important parameter affecting segmental mobility in the graft copolymer. $M_n(\text{segment})$ can be calculated by assuming that the distance between grafts is equal (i.e. $w = x = y = z$ in figure 5.1). Therefore,

$$M_n(\text{segment}) = \frac{M_n(\text{backbone})}{(1 + N_g)} \tag{5.2}$$

Figure 5.5 illustrates the variation of $M_n(\text{segment})$ with $N_g$ for Poly(4-vinylpyridine)-graft-PS copolymer. The backbone segments decrease as the number of grafts per chain increases.

5.4.2 Estimation of Reactivity Ratios

Reactivity ratios were determined using Jaacks and linear least-squares approximation methods.

5.4.2.1 The Jaacks Method

The molar concentration of a macromonomer in a copolymerisation is low. Therefore, it is possible to assume that propagation of radicals occurs predominantly via comonomer radicals (see section 2.7.2). The copolymerisation equation strictly only applies at low conversions, and data presented in table 5.6 for higher conversions are somewhat different. Jaacks proposed that the molar ratio $d[M_1]/d[M_2]$ in the copolymer should not exceed $>20/1$ for the simplification to apply. In the present work, however, this condition does not apply for all cases. An average value for $r_1$ ($\bar{r}_1$) has been calculated using only valid data. Cameron and Chisholm have proposed that determined $r_1$ values are only apparent which are related to real $r_1$ values by the relationship,
FIGURE 5.4

VARIATION OF COPOLYMER BACKBONE MOLAR MASS WITH MACROMONOMER FEED RATIO

- poly(2-VP)-graft-PS
- poly(4-VP)-graft-PS

$M_n$ (kg mol$^{-1}$)

%wt FEED MACROMONOMER
FIGURE 5.5

VARIATION OF Ng WITH SEGMENT MOLAR MASS

- poly(2-VP)-graft-PS
- poly(4-VP)-graft-PS

Ng vs. Molar Mass for poly(2-VP)-graft-PS and poly(4-VP)-graft-PS.
TABLE 5.6
MONOMER REACTIVITY RATIOS DETERMINED BY THE JAACK'S METHOD FOR THE COPOLYMERISARION OF PS MACROMONOMER (M2) AND 2-VINYLPYRIDINE (M1)

<table>
<thead>
<tr>
<th>Code</th>
<th>Conversion</th>
<th>((d[M_1]/d[M_2])^2)</th>
<th>(r_1)</th>
<th>(\bar{r}_1)</th>
<th>(r_1(\text{real}))</th>
<th>(\bar{r}_1(\text{real}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>G6A</td>
<td>6</td>
<td>414</td>
<td>2.06</td>
<td>2.05</td>
<td></td>
<td></td>
</tr>
<tr>
<td>G6B</td>
<td>5</td>
<td>149</td>
<td>1.98</td>
<td>2.02</td>
<td></td>
<td></td>
</tr>
<tr>
<td>G6C</td>
<td>6</td>
<td>98</td>
<td>1.90</td>
<td>1.88</td>
<td></td>
<td></td>
</tr>
<tr>
<td>G6D</td>
<td>8</td>
<td>65</td>
<td>2.21</td>
<td>2.04</td>
<td>2.18</td>
<td>2.02</td>
</tr>
<tr>
<td>G7A</td>
<td>54</td>
<td>320</td>
<td>1.35</td>
<td>1.34</td>
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<td></td>
</tr>
<tr>
<td>G7B</td>
<td>50</td>
<td>156</td>
<td>1.86</td>
<td>1.84</td>
<td></td>
<td></td>
</tr>
<tr>
<td>G7C</td>
<td>46</td>
<td>111</td>
<td>1.99</td>
<td>1.98</td>
<td></td>
<td></td>
</tr>
<tr>
<td>G7D</td>
<td>45</td>
<td>69</td>
<td>1.96</td>
<td>1.79</td>
<td>1.93</td>
<td>1.77</td>
</tr>
<tr>
<td>G12A</td>
<td>40</td>
<td>151</td>
<td>1.66</td>
<td>1.65</td>
<td></td>
<td></td>
</tr>
<tr>
<td>G12B</td>
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<td>53</td>
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<td>1.70</td>
<td></td>
<td></td>
</tr>
<tr>
<td>G12C</td>
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<td>28</td>
<td>1.53</td>
<td>1.64</td>
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<td>32</td>
<td>*15</td>
<td>1.48</td>
<td>1.39</td>
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<td></td>
</tr>
</tbody>
</table>

NB
1 conversion determined gravimetrically
2 determined by \(^1\)H nmr
* outside applicable conditions for Jaacks Method (continued)
TABLE 5.6 (continued)

MONOMER REACTIVITY RATIOS DETERMINED BY THE JAACK'S METHOD
FOR THE COPOLYMERISATION OF PS MACROMONOMER ($M_2$)
AND 4-VINYLPYRIDINE ($M_1$)

<table>
<thead>
<tr>
<th>Code</th>
<th>Conversion $^1$</th>
<th>$(d[M_1]/d[M_2])^2$</th>
<th>$r_1$</th>
<th>$\bar{r}_1$</th>
<th>$r_1$(real)</th>
<th>$\bar{r}_1$(real)</th>
</tr>
</thead>
<tbody>
<tr>
<td>G4A</td>
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<td>514</td>
<td>2.28</td>
<td>2.28</td>
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<td></td>
</tr>
<tr>
<td>G4B</td>
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<td>201</td>
<td>2.05</td>
<td>2.04</td>
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<td></td>
</tr>
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<td>2.29</td>
<td></td>
<td></td>
</tr>
<tr>
<td>G4D</td>
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<td>67</td>
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<td>2.19</td>
<td>2.07</td>
<td>2.17</td>
</tr>
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<tr>
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<td></td>
</tr>
<tr>
<td>G5C</td>
<td>65</td>
<td>99</td>
<td>1.85</td>
<td>1.84</td>
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<td></td>
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<td>1.77</td>
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</tr>
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<td>1.81</td>
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<td></td>
</tr>
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<td>1.89</td>
<td>1.92</td>
<td>1.85</td>
<td>1.89</td>
</tr>
<tr>
<td>G11D</td>
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<td>*17</td>
<td>1.69</td>
<td>1.59</td>
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</tr>
</tbody>
</table>

NB
1 conversion determined gravimetrically
2 determined by $^1$H nmr
* outside applicable conditions for Jaacks Method  (continued)
### TABLE 5.6 (continued)

**MONOMER REACTIVITY RATIOS DETERMINED BY THE JAACK'S METHOD FOR THE COPOLYMERISARION OF PS MACROMONOMER ($M_2$) AND N-(VINYL BENZYL)PYRROLIDONE ($M_1$)**

<table>
<thead>
<tr>
<th>Code</th>
<th>Conversion $^1$ (d[$M_1$]/d[$M_2$])</th>
<th>$r_1$</th>
<th>$\bar{r}_1$</th>
<th>$r_1$(real)</th>
<th>$\bar{r}_1$(real)</th>
</tr>
</thead>
<tbody>
<tr>
<td>G13A</td>
<td>15</td>
<td>1.45</td>
<td>1.43</td>
<td></td>
<td></td>
</tr>
<tr>
<td>G13B</td>
<td>13</td>
<td>1.35</td>
<td>1.40</td>
<td>1.31</td>
<td>1.37</td>
</tr>
<tr>
<td>G13C</td>
<td>12</td>
<td>1.37</td>
<td>1.37</td>
<td>1.28</td>
<td></td>
</tr>
<tr>
<td>G13D</td>
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<td>0.99</td>
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<td></td>
</tr>
<tr>
<td>G14A</td>
<td>64</td>
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<td>1.38</td>
<td>1.32</td>
<td>1.35</td>
</tr>
<tr>
<td>G14B</td>
<td>56</td>
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<td>1.38</td>
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</tr>
<tr>
<td>G14C</td>
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<td>0.86</td>
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</tr>
<tr>
<td>G14D</td>
<td>44</td>
<td>1.11</td>
<td>0.86</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

NB

1 conversion determined gravimetrically
2 determined by $^1$H nmr

* outside applicable conditions for Jaacks Method
\[ r_1(\text{app}) = r_1(\text{real}) + \frac{[M_2]}{[M_1]} \]  

(5.3)

where \( r_1 = r_1 \) in equation 2.20. Values for \( r_1(\text{real}) \) are also shown in table 5.6. Values of \( r_1(\text{real}) \) account for the errors produced from differences in copolymer composition in equation 2.20, thereby, allowing direct comparison of all \( r_1(\text{real}) \) values. From the data in table 5.6 \( r_1(\text{real}) \) is close to \( r_1(\text{app}) \) for each set of data if it meets the conditions stipulated by Jaacks. For data at higher conversions an integrated form of equation 2.20 should be used, provided that the excess of \( M_1 \) over \( M_2 \) is large over the whole copolymerisation. Muhlbach and Percec carried out copolymerisations of poly(ethylene oxide) macromonomers with methacrylate comonomers. The reactivity ratios were obtained by a single-point Jaacks experiment at different conversions. The reactivity ratios were found to be conversion dependent, and it was proposed that this was due to different induction periods for the macromonomer and comonomer. Vinyl pyridine copolymers show a similar trend with reactivity ratios varying with conversion. As stated in section 2.7.3, the drift in feed composition with increasing conversion is low compared to conventional statistical copolymerisations. Therefore, an integrated form of equation 2.20 was not used.

5.4.2.2 Linear Least-squares Methods

Fineman-Ross\textsuperscript{136} and Kelen-Tudos\textsuperscript{137} methods were used to determine reactivity ratios for graft copolymerisations. The values can be directly compared to the values obtained for analogous statistical copolymerisations using styrene and comonomer (see table 5.7). The values of \( r_1 \) determined for copolymerisations at intermediate and high conversions are not strictly correct; an integrated form of the copolymer equation should be used. The values predicted by Fineman-Ross and Kelen-Tudos methods are similar for the same set of data. The \( r_1 \) values determined by the Jaacks method also agree with the linear least-squares methods, if the data outside the
<table>
<thead>
<tr>
<th>Code</th>
<th>Conversion</th>
<th>Type</th>
<th>Fineman-Ross</th>
<th>Kelen-Tudos</th>
<th>Jaacks</th>
</tr>
</thead>
<tbody>
<tr>
<td>G4</td>
<td>8</td>
<td></td>
<td>2.29 1.00</td>
<td>2.25 .99</td>
<td>2.17</td>
</tr>
<tr>
<td>G5</td>
<td>65</td>
<td>4-VP</td>
<td>1.63 1.00</td>
<td>1.67 .99</td>
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</tr>
<tr>
<td>G11</td>
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<td></td>
<td>2.07 1.00</td>
<td>2.05 1.00</td>
<td>1.89</td>
</tr>
<tr>
<td>G6</td>
<td>7</td>
<td></td>
<td>2.06 1.00</td>
<td>2.03 .99</td>
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</tr>
<tr>
<td>G7</td>
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<td>2-VP</td>
<td>1.24 1.00</td>
<td>1.32 .96</td>
<td>1.77</td>
</tr>
<tr>
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<td>35</td>
<td></td>
<td>1.69 1.00</td>
<td>1.72 1.00</td>
<td>1.56</td>
</tr>
<tr>
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<td>VBP</td>
<td>1.47 1.00</td>
<td>1.45 1.00</td>
<td>1.37</td>
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<tr>
<td>G14</td>
<td>55</td>
<td></td>
<td>1.43 1.00</td>
<td>1.43 1.00</td>
<td>1.35</td>
</tr>
</tbody>
</table>

NB  
conversion is average of all copolymerisations in a series  
corr. = correlation coefficient for linear least squares methods
applicable range of conditions are ignored. Therefore, the Jaacks analysis is justified in assuming that $r_2$ can be neglected in macromonomer copolymerisations. The values of $r_1$ are found to vary with increasing conversion for vinylpyridine copolymerisations. This may be due to different induction periods for the macromonomer and comonomer or to a small drift in feed composition with increasing conversion. Values of $r_2$ have not been quoted as they are subject to large errors in their determination due to the low molar concentration of macromonomers used. It is possible to determine $r_2$ values where the molar mass of the macromonomers is very low or when the mole fraction of macromonomer in the feed and the copolymer is high.

The three methods used to determine comonomer reactivity ratios in the present work are all based on the copolymerisation equation (equation 2.12). This equation represents the instantaneous behaviour of the copolymerisation and, therefore, can only be used at low conversions where little or no change in the feed composition is observed. Typically, for conventional statistical copolymerisations, conversions are 5% or less. For graft copolymerisations, minimum conversions are significantly higher because little or no change in the feed composition is observed. Previous work in this laboratory\textsuperscript{18} has shown only small changes of feed composition at higher than 40% conversion.

The copolymerisation equation is based on the terminal model. It is assumed that the reactivity of the propagating radical depends only on the monomer unit at the end of the copolymer chain at which the radical is located. It is also assumed that the molar masses of the copolymers are high and negligible amounts of monomer are consumed in initiation and termination. In the present work, the terminal model is assumed to apply, although the molar masses of the graft copolymers are not very high. This implies that the reactivity of the macromonomer radical is the same as styrene, with no contribution from the
macromonomer chain. When the data obtained from statistical and graft copolymerisations are compared a significant difference in $r_1$ values is observed. Therefore, the macromonomer chain does alter the reactivity of the propagating radical. The terminal model is therefore not the most accurate model for copolymerisation in the present work. Compositional data alone is inadequate for discriminating between the various models. Comonomer sequence distributions are much more sensitive to the chain growth processes which separate the various models.

The linear least-squares methods for determining reactivity ratios are statistically invalid. It is assumed in linear least squares, that there are no errors in the independent variable (i.e. the feed composition) and that the dependent variable errors are normally distributed and statistically random. This assumption is incorrect since redefining $M_1$ to $M_2$ can lead to different values of $r_1$ and $r_2$. However, such redefining for the graft copolymerisations has negligible effect on the values of the comonomer reactivity ratio. Values for reactivity ratios are only approximate estimates. Non-linear least squares analysis should provide better treatment of data allowing correct weighting and some estimate of precision. For graft copolymerisations it is difficult to meet the criteria for non-linear least squares analysis as a high weight fraction of macromonomer is required in the feed. The unreacted macromonomer can then prove difficult to remove completely. Asami et al. have determined values of both $r_1$ and $r_2$ by using UV spectroscopy to measure compositions of poly(2-vinylnaphthalene)-graft-poly(tetrahydrofuran) copolymers. Most reports in the literature only quote values of $r_1$ determined by a Jaacks simplification or a linear least squares analysis, despite their shortcomings.

5.4.3 Macromonomer Reactivity

The comonomer reactivity ratio ($r_1$) is defined by
\[ r_1 = \frac{k_c c}{k_m c} \quad c = \text{comonomer} \]
\[ k_c c \quad m = \text{macromonomer} \]
\[ * = \text{radical} \]

The reactivity ratio gives information about relative differences in rate constants for a propagating comonomer radical adding macromonomer instead of another comonomer unit.

Values of \( r_1 \) for graft copolymerisations are almost twice the values of conventional statistical copolymerisations. The rate of addition of comonomer is almost twice as fast or the rate of addition of macromonomer is halved compared to styrene. If the rate of addition of macromonomer is reduced, it can be concluded that the rate constant for a propagating macromonomer radical adding another macromonomer unit will be lower. Thus, \( r_2 \) which is defined as

\[ \frac{i}{r_2} = \frac{k_m c}{k_m m} \]

will also be lowered. Therefore, the reactivities of propagating radicals are not just governed by resonance, steric and polar effects associated with the chemical structure of the end group. This work agrees with work performed by Ito et al\(^{196}\) on the copolymerisation of methacrylate-terminated PS macromonomer \((M_n=3.2\times10^3 \text{g.mol}^{-1})\) with hydroxyethylacrylate \((M_1)\) in DMF as solvent. It was found that the reactivity of the macromonomer was lower compared to methylmethacrylate. This conflicts with work by Tsukahara et al\(^ {197}\) who copolymerised methacrylate-terminated PS macromonomer \((M_2, M_n=12.4\times10^3 \text{g.mol}^{-1})\) with styrene and MMA \((M_1)\) using benzene as a solvent. They showed that the macromonomer reactivity was similar to conventional methacrylates. It was also predicted that partial segments of PS and PMMA would be compatible at a concentration of 33% (w/v) in benzene, providing the degree of polymerisation was below 110. The present work was carried out with a total monomer concentration of 20% (w/v) in DMF. No information is
known on the compatibility of the various comonomers with PS in DMF, but there may be some incompatibility of the interacting segments in the copolymerisation as it proceeds. The nature of the solvent has shown to be extremely important. Tsukahara et al.\textsuperscript{167} showed that for the copolymerisation of a methacrylate-terminated PS macromonomers with MMA in cyclohexane, a good solvent for PS (at the polymerisation temperature) but a poor solvent for PMMA, the macromonomer reactivity was reduced in comparison to its reactivity in benzene, a good solvent for both components. This reduced reactivity was due to the decrease in interpenetration of the PS and PMMA segments in cyclohexane.

Takaki and Asami\textsuperscript{198} have determined reactivity ratios for both $r_1$ and $r_2$. Styryl-terminated PS macromonomers were copolymerised with MMA in benzene. For the macromonomer with $M_n = 3.0 \times 10^3$ g mol$^{-1}$, $r_1$ was comparable to conventional model copolymerisations whereas $r_2$ was lower. However, for the macromonomer with $M_n = 6.0 \times 10^3$ g mol$^{-1}$, $r_1$ and $r_2$ were lower than conventional copolymerisations. Asami also found that $r_2$ was significantly lower than conventional copolymerisations. The copolymerisation of macromonomer $M_2$ with a conventional comonomer $M_1$ depends upon the following reactions.

\begin{align*}
  k_{11} \quad \text{(branched or linear) polymer radical} \ + \ \text{small comonomer} \\
  k_{12} \quad \text{(branched or linear) polymer radical} \ + \ \text{macromonomer} \\
  k_{22} \quad \text{$\omega$-branched polymer radical} \ + \ \text{macromonomer} \\
  k_{21} \quad \text{$\omega$-branched polymer radical} \ + \ \text{small comonomer}
\end{align*}
It may be assumed that rate constants $k_{ii}$ and $k_{i'i'}$ which are defined for growing polymer radicals and small comonomers, are of equal reactivity compared to conventional copolymerisations. However, $k_{12}$ and $k_{22}$ are expected to be much lower than for conventional copolymerisations because the addition reaction between a polymeric radical and a long chain monomer. If we consider the position of the growing radical, in $k_{22}$ the propagating radical cannot be at the end of a chain. Thus, the hindering effect is greater for $k_{22}$ than $k_{12}$. Therefore, values of $r_2$ are expected to be lower and $r_1$ to be slightly increased compared to conventional copolymerisations. In the present work, only values of $r_1$ have been determined, but by use of the argument above it can be inferred that the macromonomer reactivity is reduced compared to conventional copolymerisations. The reduction in macromonomer reactivity may be attributable to DMF being a poor solvent for PS chains.

5.5 PREPARATION OF MICELLAR DISPERSIONS

The ability of block and graft copolymers composed of incompatible segments to form micelles in solution was discussed in section 2.2.3. Graft copolymers form associated aggregates or micelles in equilibrium with free, unassociated graft copolymer. If a graft copolymer is dissolved in a selective solvent for one of the segments, this equilibrium is moved towards the aggregated form. As the molar mass of the insoluble segment increases relative to the soluble block, the equilibrium increasingly favours the aggregated structure. At high ASB values, virtually all the copolymer chains are present as associated micelles. The critical micelle concentration (cmc) will also be progressively reduced as the ASB value increases. The core size of such micelles is governed by the molar mass of the insoluble segment, and the surface area which the soluble segment is capable of stabilising (see equations 2.6 and 2.7). For graft copolymers the number of soluble segments where these are grafts and their average distance apart are also critical in determining micelle size. The fringe
thickness of micelles is largely determined by the length (i.e. molar mass) of the soluble segment.

Micellar dispersions of poly(4-VP)-graft-PS, poly(2-VP)-graft-PS and Poly(VBP)-graft-PS have been prepared in cyclohexane, toluene and methanol. All micellar dispersions were at a concentration of 3% by weight of copolymer. No attempt was made to study the effect of concentration on micelle structure or the determination of the cmc. The concept of anchor to soluble balance where used refers to values determined assuming the PS grafts are the soluble stabilising block. This is not the case in methanol based systems, but the values have not changed in order to prevent confusion.

5.5.1 Micellar Dispersions in Cyclohexane and Toluene

Micellar dispersions in cyclohexane and toluene have a 'hairy' structure with the core composed of insoluble backbones and the soluble grafts conferring stability. Stable micellar dispersions could not be produced with very high ASB values, i.e. G11A (ASB = 5.8:1), G12A (ASB = 4.8:1) and G14A (ASB = 5.5:1) in cyclohexane and toluene. This is attributed to the short PS chains being unable to stabilise the large core produced by VP or VBP segments in cyclohexane and toluene.

Micellar dispersions were successfully prepared using the other graft copolymers; results are shown in table 4.12. Transmission electron microscopy showed that the spherical particles produced in the dispersion medium were of a narrow particle size distribution (see figure 4.4 & 4.5). Particle size was also determined by TEM.

MD16 (G14C in cyclohexane) as illustrated in figure 4.5 contained long rod-like micelles (125x8 nm). No other graft copolymers showed similar behaviour. Price et al demonstrated metastable worm-like micelles for a polystyrene-b-polyisoprene copolymer in N,N-dimethylacetamide, on heating though the micelles reverted to spherical particles. The copolymer composition was found to be critical in the formation of these
worm-like micelles. In the present work, the micellar dispersions were heated to remove residual dichloromethane; they are not, therefore, metastable. It is thought that the rods are composed of an insoluble core of a number of backbone segments aggregated together with the grafts pointing into the dispersion medium at all angles.

SAXS provided an alternative method of determining the dimensions of the micelles using the method established by Guinier\textsuperscript{168,169} for determining the radius of gyration (see section 2.8.1). The largest errors incurred in calculating the radius of gyration are in the desmearing process. Overall, the experimental error for the determination of $R_g$ will be between 5-10%. Broadbent, Brown and Dawkins\textsuperscript{199} have studied a poly(dimethylsiloxane)-block-PS copolymer in dodecane and octamethylcyclotetrasiloxane they confirmed experimentally that $R_g$, as determined by the Guinier method, is not influenced by the micellar fringe. They determined $R_g$ in octamethylcyclotetrasiloxane with an electron density matched to the fringe (i.e. the soluble segment of the copolymer), and in dodecane with a different electron density to the soluble segment. It was found that the value of $R_g$ did not change, and that in the matched electron density experiment the data followed Porod's law. In the present work (see table 4.12), matched electron density experiments were also performed using oligostyrene as the dispersion medium, matching the electron density of the soluble PS graft segments. No negative deviations were found from Porod's Law indicating that the fringe did not contribute to the scattering data. Therefore, the $R_g$ value determined using the Guinier method gave the dimensions of the core. Other literature interpreting the value of $R_g$ offers conflicting views. Malhotra and Bluhm\textsuperscript{200} using slit smeared intensities suggested that $R_g$ was determined from two Guinier plots, one for a core and the other for the whole micelle. Strictly, the Guinier method must be used with desmeared intensities. Roe and Rigby\textsuperscript{201} using a polybutadiene-
block-PS copolymer in low molar mass polybutadiene determined the value of $R_g$ by two independent methods, one being Guinier analysis. Both methods gave micelle core volumes which agreed well using desmeared intensities. Plesčíl and Baldrian\textsuperscript{202} studied a PS-block-polybutadiene copolymer (24\% wt PS) in heptane. The Guinier method was used to determine the radius of gyration using desmeared intensities. A guinier plot with two slopes was observed, this was assumed to be due to the core radius and the overall micelle radius. The degree of swelling by heptane in the core was also determined. The size of the core is small compared to the fringe thickness and therefore the micellar dispersion is not an ideal two phase system as in previous work\textsuperscript{199,201}. Guinier analysis is generally only applicable to two phase systems.

Reasonable agreement is observed between the two methods (see table 4.12). TEM data are obtained on dry micelles, i.e. the dispersion medium has been removed. Thus, the stabilising PS graft layer has collapsed onto the surface of the micelle core. No account is taken of the thickness of this collapsed layer in determining the micelle core diameter. This error may be quite large with small micelle cores with a collapsed layer of approximately 1-2nm. The core of the micelle may alter in size and shape upon removal of the dispersion medium as well, if the core was swollen with diluent, leading to further errors. Other errors in the determination of core diameters are discussed in section 5.7. SAXS data are obtained without altering the structure of the micelle i.e. it is a non-invasive technique. Although it is easier to obtain results directly from TEM, the effects of sample preparation cannot be ignored in the analysis of the results. It is believed that SAXS data provide accurate results on core size which TEM cannot provide. TEM can be utilised to observe relative differences between micelle structure and size. There are only a few examples in the literature on the study of micelles composed of graft copolymers. Horii et al\textsuperscript{203} studied micelles formed by
poly(vinyl acetate)-graft PS copolymers in ethyl acetoacetate a poor solvent for PS using TEM. The large size distribution was attributed to the polydispersity of the graft copolymers. Price and Woods\textsuperscript{204} studied the viscosity and light scattering behaviour of a polystyrene-graft-polyisoprene copolymer in n-decane and methylcyclohexane. They observed that the micelle molar mass increased with decreasing temperature in both systems. But, the molar mass in methylcyclohexane above 278K indicated monomolecular micelles.

The determination of fringe thickness is subject to large errors due to a number of factors. Firstly, fluctuations in the electron density of the core will lead to positive deviations from Porod's Law. And Secondly, the statistical spread of the scattering data is large at high angles because of the small amounts of scatter involved (standard deviation of scattered intensities = \(\text{counts}^{0.5}\)). The last source of errors is the subtraction of background scattering data. If too large a subtraction of background is used, then larger than expected negative deviations are observed.

Calculation of fringe thickness relies on models of the electron density profile of the fringe. Two models have been used, namely a linear and a sigmoidal profile (see section 2.8.2). There are a number of mathematical approximations to these two models, but these are only applicable over a limited range of scattering angles. The Vonk and empirical approximations for a linear and sigmoidal electron density profile respectively have been used. The ranges of applicability are shown below.

\[
\text{Vonk} \quad \delta_s < 0.10 \\
\text{Empirical} \quad 0.009 < \delta_s < 0.72 \quad \delta = 120.5 \delta
\]
The Vonk approximation does not lie within the range but is used for comparison. A more detailed analysis of the various methods can be found elsewhere.\(^{179}\)

The values obtained for the fringe thicknesses of micellised graft copolymers are shown in table 4.12. These values are compared in table 5.8 to theoretical data for PS dimensions for coiled and extended conformational states. \(\langle r^2 \rangle^{0.5}\) which is defined by the root-mean-squared end-to-end distance of the polymer chain and \(L_{\text{max}}\) which is the extended chain length. The characteristic ratio \(\langle r^2 \rangle / n l^2\) is 9.85 for PS in a theta solvent\(^ {191}\), where \(n\) is the number of main chain bonds and \(l^2\) is the mean-square bond length. \(L_{\text{max}}\) is an extended chain length assuming that a reasonable conformation is that found in the crystal lattice and that sensible bond lengths, angles and conformational energies are observed. Thus, the conformation of a polystyrene chain is a helix having repeat units every 3 monomer units and a repeat distance of 0.665 nm\(^ {191}\). For poly(4-VP)-graft-PS copolymers at low graft frequencies, the fringe thickness is comparable to the root mean squared end-to-end distance for an unperturbed chain of PS. It has been demonstrated that short chain polymers have a similar size in both good and theta solvents\(^ {205}\). For MD19 (G11D in toluene), the fringe thickness is calculated to be only 2.2nm. It has been assumed in the discussion so far that the soluble grafts provide stabilisation of the micelles and the grafts do not contribute to the micelle core. At high graft frequencies the mean distance between grafts is small (only 15 backbone repeat units between grafts) assuming the chain model in figure 5.1. Therefore, complete solvation of the PS grafts may not occur. This model would predict a micelle core composed of poly(4-vinylpyridine) with an outer shell of unsolvated PS and then a fringe of soluble PS grafts. Alternatively, the core is composed of a mixture of insoluble backbone and a few PS grafts, leading to a heterogeneous core structure and the remainder of the grafts providing stabilisation. Experiments
TABLE 5.8
THE CHAIN DIMENSIONS OF PS $M_n=3.2$ kg mol$^{-1}$
IN VARIOUS CONFORMATIONS$^{192}$

<table>
<thead>
<tr>
<th>Dimension</th>
<th>Value</th>
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</thead>
<tbody>
<tr>
<td>$&lt;r^2_o&gt;^{1/2}$</td>
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<td>$L_{max}$</td>
<td>6.82 nm</td>
</tr>
<tr>
<td>$&lt;s^2&gt;^{1/2}$</td>
<td>1.55 nm</td>
</tr>
<tr>
<td>$&lt;v^2_v&gt;^{1/2}$</td>
<td>8.08 nm</td>
</tr>
</tbody>
</table>
performed using oligostyrene would match the electron density of the grafts but not of any PS grafts in the micelle core as it is in the bulk state. Porod's law plots of MD40 (G11D in oligostyrene) showed some positive deviations indicating that the micelle core does not have a homogeneous electron density profile, while MD39 (G11B in oligostyrene) showed no such positive deviations. Guinier plots of MD40, MD19 and MD20 showed the presence of some ripples; this is indicative of either monodisperse particles or the presence of a two layer structure in the micelle core. The amount of rippling would be dependent on the degree of ordering of these layers in the micelle core. Monodisperse particles are not evident from TEM of MD20, although there is a narrow particle size distribution. It is believed that the PS grafts in the micelle core are nearer the surface leading to a heterogeneous electron density profile and an enriched PS layer near the core surface. If the above assumptions are correct, a subtraction due to the PS in the core may be made in order to determine the volume attributable to poly(4-vinylpyridine). This subtraction is not easily performed as the electron density profile of the fringe and core need to be known. The density of the fringe is also required which is difficult to determine experimentally.

The number of copolymer molecules involved in the formation of one micelle (the micellisation number) was calculated from equation 2.7. It was assumed that the core of poly(4-VP) was not significantly swollen by solvent and that the density of the core was 1.10 g/cm³. The area stabilised by each PS graft was obtained by equation 2.6. The average distance between grafts was also calculated assuming that each graft stabilised a hexagonal area centred around the terminally anchored graft. The results determined by TEM and SAXS are compared in table 5.9. The micellisation number, area stabilised per graft and the distance between grafts all decrease with increasing graft frequency. Further discussion on the area stabilised per graft and the average distance between grafts are in section 5.7.1.
<table>
<thead>
<tr>
<th>Graft Code</th>
<th>Copolymer</th>
<th>Diluent</th>
<th>( R_{sp} )</th>
<th>( n )</th>
<th>Area Stabilised</th>
<th>( d )</th>
<th>( R_{sp} )</th>
<th>( n )</th>
<th>Area Stabilised</th>
<th>( d )</th>
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<td>2.21</td>
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<td>1.81</td>
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<td>1.62</td>
<td>10.2</td>
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<tr>
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<td>2.15</td>
<td>1.58</td>
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<td></td>
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<td>28</td>
<td>1.53</td>
<td>1.33</td>
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</tr>
<tr>
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<tr>
<td>MD23</td>
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</tr>
</tbody>
</table>

NB \( n \)=micellisation no. \( R_{sp} \)=radius of micelle core in nm, \( d \)=distance between stabilising grafts.
Figure 5.6 demonstrates the dependence of micelle core radius with copolymer composition. Figure 5.7 shows the variation of the area stabilised with anchor to soluble balance; a linear relationship is observed for all systems except for poly(4VP)-graft-PS in toluene. This deviation may be explained if some of the PS grafts are contributing to the micelle core thus, reducing the number of grafts available to stabilise the micelle.

Micelles of poly(VBP)-graft-PS in toluene all showed positive deviations from Porod's law. These graft copolymers can be considered to be composed of polystyrene backbones and grafts with pendant pyrrolidone groups attached to the backbone repeat units. At high graft frequencies, the number of pyrrolidone units is low (approximately 30 pyrrolidone units compared to 350 styrene units). True micellisation may not occur with only loose aggregates of the graft copolymers in solution since poly(VBP) swells in toluene. The Guinier plot may represent the radius of gyration for the whole molecule. No evidence of micelles was observed using TEM, indicating that either film formation occurred or the graft copolymers did not form multimolecular micelles. In cyclohexane, spherical micelles were observed for G14B (see figure 4.5); whereas G14C formed rod-like micelles. Poly(VBP) homopolymer does not swell appreciably in cyclohexane, therefore multimolecular micelles are formed which are visible by TEM. MD26 (G14D in cyclohexane) has only 4 repeat units between grafts; it is therefore unlikely to form multimolecular micelles.

5.5.2 Micellar Dispersions in Methanol

Dispersions in methanol consist of insoluble grafts being stabilised by soluble backbone segments conferring stability by loops and tails. Stable micellar dispersions could not be made with G11D, G12D and G14B,C,D. The loops and tails of VP and VBP are not large enough to protect the insoluble PS grafts.
FIGURE 5.6

DEPENDENCE OF MICELLE CORE RADIUS ON $M_n \text{(segment)}^{1/2}$

poly (4VP)-g-PS by SAXS, poly (2VP)-g-PS by TEM

- poly (2VP)-graft-PS/cyclohexane
- poly (4VP)-graft-PS/Toluene
- poly (4VP)-graft-PS/cyclohexane
Figure 5.6 (Continued)

Dependence of micelle core radius on $M_n(\text{segment})^{1/2}$ by TEM

- poly(4VP)-g-PS/cyclohexane
- poly(2VP)-g-PS/cyclohexane
FIGURE 5.7

VARIATION OF AREA STABILISED PER GRAFT WITH ASB
FOR MICELLAR DISPERSIONS

- Poly(2VP)-g-PS/Cyclohexane TEM
- Poly(4VP)-g-PS/Cyclohexane TEM
- Poly(4VP)-g-PS/Cyclohexane SAXS
+ Poly(4VP)-g-PS/Toluene SAXS
Stable micellar dispersions were characterised by TEM and SAXS (see table 4.12). TEM showed that spherical particles with a narrow size distribution had been produced (see figure 4.6). The optical density of the particles was observed to increase with increasing number of grafts in the copolymer. As the number of grafts in the copolymer increases, the number of insoluble graft segments per copolymer also increases. The micelle size determined by TEM was constant for different copolymer compositions.

SAXS was also used to determine micelle size and structure. Plots according to Porod's law showed marked positive deviations when the copolymer architecture was low in grafts. As the composition of the copolymer becomes richer in grafts, the deviations are smaller and eventually become slightly negative. Therefore, the micelle core does not have a constant electron density profile, although the effect is not so pronounced for dispersions of copolymer with high graft frequency. The calculation of a fringe thickness for the micelles will not yield accurate values because it is not possible to account for the effect of a heterogeneous core. The determination of the radius of gyration was performed using the Guinier method. The value of $R_g$ was found to be approximately constant for different copolymer compositions.

For the graft copolymers in methanol, the PS segments are expelled from the methanol thus leading to association. The free energy of the soluble segments increases whilst the PS segments will decrease. As a consequence of the reduction of the interfacial area between the PS segments and the methanol, the total free energy is also reduced. This minimisation of free energy determines the size, structure and shape of micelles. If we consider the formation of a core consisting only of PS graft segments, the core radius would not exceed 4nm if the micelles are spherical. This is equivalent to the unperturbed dimensions for a PS chain of $M_n=3.2 \text{ kg.mol}^{-1}$ (see table 5.8). In the present work, the micelle radius is
approximately 8-9nm. Therefore, the core of the micelle must be composed of other components. If the core is composed of different components of different electron densities in a segregated state, this will give positive deviations from Porod's law. For the requirement to minimalise the free energy of the graft copolymer in solution, the PS segments need to be encased in a shell of soluble backbone segments. A number of geometric models may fit the observed data, these are discussed below.

Firstly, the shell may form a bilayer in order to completely encase all the PS graft segments as shown in figure 5.8a. This core of the micelle can be visualised as a hollow sphere or spherical vesicle. The centre and outer fringe of the micelle is composed of solvated backbone segments encasing insoluble PS graft segments. A number of theoretical scattering curves using SAXS have been published for hollow spheres and spherical vesicles. The predicted scattering curves assume a perfectly monodisperse system of particles. A curve shows high frequency oscillations modulated with a low frequency (see figure 5.8b). The high frequency oscillations depend on the dimensions of the vesicle and these oscillations are appreciably reduced when the vesicles have a size distribution. The low frequency oscillations is dependent on the electron density profile. For micellar dispersions with lowest grafts per chain, a number of high frequency oscillations are observed. Figure 5.8a shows the expected behaviour with increasing graft content in the copolymer assuming the bilayer model is valid for all compositions. Similar behaviour will probably not be observed with a diblock copolymer of PS-b-poly(4-VP), because the block copolymer will form a 'hairy' micelle. A multiblock copolymer consisting of a number of A-B blocks with segments of similar dimensions to the PS grafts may form a similar type of hollow sphere micelle.
FIGURE 5.8
PROPOSED MODELS FOR MICELLES OF POLY(VP)-GRAFT-PS IN METHANOL

(a) low grafts ------> high grafts

---- PS grafts ---- poly(VP) backbone

(b) theoretical scattering curve for spherical vesicle

(c) model with unsolvated backbone in the micelle core

unsolvated poly(VP) backbone (loops)
soluble poly(VP) backbone (tails)
Assuming a hollow sphere model is correct for micellar dispersions in methanol, it is possible to calculate the inner and outer radii for the micelle from \( R_g = \frac{3r_2^5 - r_1^5}{5r_2^3 - r_1^3} \) (5.8)

Alternatively, unsolvated backbone segments may contribute to the micelle core structure, as illustrated in figure 5.8c in a similar manner to MD19 (G11D in toluene). Evidence for this can be seen in the Porod's law plot showing positive deviations and the presence of rippling on the Guinier plot. Finally, true micelles may not occur for high ASB copolymers with only loose aggregates being formed, these under the TEM appear to be micellar upon removal of the dispersion medium. Therefore, for G11A, G12A and G14A in methanol, the Guinier plot may determine the radius of gyration for individual graft copolymer molecules (i.e. monomolecular micelles) in loose aggregates. With increasing graft frequency and lower copolymer backbone molar mass, multimolecular micelles are probably formed which are composed of a core of PS and unsolvated poly(VP) backbone. The stabilising layer is due to solvated poly(VP) backbone in loops and tails.

For micellar dispersions in methanol, the core size depends on the length (i.e. molar mass) of the PS grafts. Since the molar mass of the grafts have been kept constant for all copolymers, no significant variation of micellar core dimensions is observed on altering the graft frequency. In toluene and cyclohexane, the copolymer backbone varies with copolymer composition, therefore the micellar core radius changes. No data has been calculated for the area stabilised per backbone or the micellisation number in methanol because of the lack of clear evidence supporting one particular model.
5.6 NON-AQUEOUS DISPERSION POLYMERISATION OF PET

Dispersion polymerisations of condensation polymers are a useful route to producing high molar mass polymers\textsuperscript{12,61,62}. In conventional melt polymerisations the viscosity of the polymer increases rapidly with increasing molar mass, thus causing problems with reactor mixing. Reaction temperatures in dispersion polymerisations can be up to 50K lower than conventional melt reactors.

Non-aqueous dispersions of PET stabilised by graft copolymer stabilisers were prepared by condensation polymerisation as described in section 3.8.1. The reaction conditions and characteristics of the resulting dispersions are given in table 4.16. Very few stabilisers were found to be effective in stabilising dispersions of PET. Only graft copolymers containing N-(vinylbenzyl)pyrrolidone were successful, with the copolymers having a low number of grafts per chain. The particle size of the dispersions was dependent on copolymer composition and concentration. As the number of grafts in the copolymer increased, the size of the particles was reduced. As the stabiliser concentration was reduced, larger particles were formed. This is in agreement with previous work\textsuperscript{4}. As the size of the particles is reduced the proportion of surface area to volume increases, thus requiring more graft copolymer to stabilise the particles.

Other stabilisers that have proved effective in PET dispersion polymerisations include PMMA-co-poly(glycidylmethacrylate)-co-poly(12-hydroxystearic acid), PMMA-graft-polybutadiene, PMMA-co-poly(12-hydroxystearic acid) and poly(vinylpyrrolidone)-graft-C\textsubscript{14}-C\textsubscript{18} alkyl chain\textsuperscript{207}. The stabilisers containing epoxide or ester groups will be susceptible to chemical grafting to the particle by either ring opening of the epoxide or transesterification. Ring opening of pyrrolidone is well documented\textsuperscript{208} in mineral acids at room temperature. In the presence of bases polyvinylpyrrolidone forms crosslinked gels at 373K. It may be possible that at
523+K in a dispersion polymerisation that ring opening of the lactam ring may occur with the formation of an ester linkage to the particle. If this reaction was to occur on a 1% yield over the time of the polymerisation, then it is probable that on average all the pyrrolidone backbones will be chemically grafted to the particle by at least 1 ester linkage per chain. Therefore, all stabilisers used for PET dispersions polymerisations are probably chemically bound to the PET particle. It is thought that at the high shear rates and high temperatures in the reactor, purely physically adsorbed stabilisers will not be effective as the anchoring mechanism will be to weak. This hypothesis is backed up by the use of polyvinylpyridine graft copolymers which cannot be chemically bound to the PET particle, and do not confer stability on the dispersions.

Dispersion polymerisation is defined as having a reaction mixture which initially is homogeneous, but as the polymerisation proceeds polymer precipitates out and the reaction continues in a heterogeneous manner. Clearly, PET polymerisations as carried out in this work are not true dispersions. They probably are more akin to non-aqueous suspension polymerisations, where the reaction mixture is initially heterogeneous with droplets of liquid monomer but the diluent is an aliphatic hydrocarbon.

MacDonald et al. have described the use of dispersion polymerisation for synthesising main-chain thermotropic liquid-crystal polymers using a combination of hydrophobic silica and an acrylic copolymer. Stable dispersions could not be achieved by using one of the stabilisers on their own. The silica was thought to be positioned at the interface of the initial droplets. However, these small silica particles cannot maintain droplet stability particularly when the viscosity of the droplet increases rapidly. The acrylic copolymer is chemically bound to the droplet interface thereby providing further stabilisation at the most critical stage.
5.7 FREE RADICAL DISPERSION POLYMERISATION

A number of different free radical dispersion polymerisation systems have been studied. The dispersions were characterised by TEM and SEM as described in section 3.9.3. The amount of stabiliser adsorbed onto the particle surface was also determined (see table 4.17 & 4.18). The determination of dry particle size assumes that the soluble stabilising segments attached to the particle surface do not contribute to the overall particle size. This assumption is not correct as when the dispersion medium is removed the stabilising layer collapses. The contribution to the particle diameter can be neglected since this layer thickness represents less than 4% for even the smallest particles (50nm). Errors can also arise from electrical fluctuations in the microscope, which can generate up to a 5% error in the recorded magnification. Another source of possible error may result from a change in the sample during preparation of the microscope grids for TEM and sputter coating for SEM. If the particles were significantly swollen in the dispersion medium, removal of the medium may alter the particle size and shape. However, PMMA, PS or poly(vinylpyridine) particles are not thought to be swollen with diluent. Depolymerisation of the polymer particles has been reported under the hostile conditions of high vacuum and electron bombardment within an electron microscope.  

5.7.1 Dispersion polymerisation of MMA

Non-aqueous dispersions of PMMA stabilised by graft copolymer stabilisers were prepared by radical polymerisation as described in section 3.8.3. The reaction conditions and characteristics of the resulting dispersions are given in table 4.13. The calculation of the average area stabilised per graft is given in table 5.10. Dispersion polymerisations of MMA have been extensively reported using both block copolymers and graft copolymers. The Graft copolymers used in the present work have not been used previously as stabilisers.
<table>
<thead>
<tr>
<th>Code</th>
<th>Stabiliser</th>
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The rate of polymerisation was not studied, but all experiments were taken to high conversions. Typically, 80+% conversions were achieved after 2 hours. Taylor\textsuperscript{7,16} has determined the rate of dispersion polymerisation of MMA using block copolymer stabilisers. Near complete conversions were obtained within 5 hours. Particle size is dependent on a number of variables including conversion; therefore, all experiments were taken to similar conversions.

The solubility of PMMA in cyclohexane is almost negligible. Swelling of the particles was, therefore, not considered. Taylor and others\textsuperscript{4,7} observed that the plot of monomer conversion with time had a sigmoidal form. This increase in the rate of polymerisation at about 10% was a result of the gel effect. The molar masses of PMMA dispersions are shown in table 4.18. Conventional solution polymerisation of MMA under similar conditions predicts a molar mass of $2 \times 10^4$ g.mol\textsuperscript{-1}. Generally, molar masses were $1-2 \times 10^5$ g.mol\textsuperscript{-1} for PMMA dispersions indicating that the gel effect was occurring. The dispersion temperature of 342 K was chosen for all dispersions to allow the graft copolymer molecules in equilibrium between micellar dispersions and free unassociated stabiliser molecules to move towards free chains in solution.

Electron microscopy has shown that the particles of PMMA produced were spherical with a narrow particle size distribution (see figure 4.13 & 4.14). Therefore, the process of particle nucleation was rapid occurring in the early stages of polymerisation with no secondary nucleation taking place. No significant improvement in distribution was observed by using seed/feed techniques instead of one shot methods. The use of a seed stage in polymerisations did not produce significantly smaller particles. This did not agree with previous work performed at Loughborough\textsuperscript{6,7,18}. Previous work on PMMA dispersions at Loughborough has used n-heptane and n-hexane as diluents. The threshold molar mass for precipitation of growing chains is predicted to be similar for cyclohexane considering
the small difference in solubility parameters. Since MMA is a solvent for PMMA, it would be predicted that the threshold molar mass for precipitation would increase with increasing amounts of MMA in the feed. Therefore, the number of nuclei produced would be lower. Consequently, a smaller number of particles with larger diameters would be produced. Winnik et al\textsuperscript{210} have shown that by altering the solvency of the initial dispersion medium by adding variable amounts of solvent for PMMA, larger particles are produced. However, the solvency of the dispersion medium is also likely to modify the behaviour of the stabiliser. Higher solvency will reduce the tendency for the stabiliser to associate with growing polymer chains during particle formation in addition to imparting the efficiency of the anchoring mechanism of particles already formed. Therefore, it is possible that particle growth is determined by coagulation\textsuperscript{211}.

(a) Effect of Copolymer Composition on Particle Size

Graft copolymer architecture was found to be an important factor in dispersion polymerisation. For poly(2-VP)-graft-PS copolymers stable dispersions were produced with the exception of G12A (ASB = 5.8:1). Poly(4-VP)-graft-PS copolymers were not so successful with only G11D producing stable dispersions. In the case of G12A, the ASB value lies outside the predicted range for conferring particle stability because even if the graft copolymer could be micellised in the dispersion medium, the grafts are too widely spaced to provide steric stabilisation of the particle thus preventing flocculation. Although all dispersions were stable, micrographs of G12B stabilised dispersions show evidence of bridging between particles under the TEM and SEM (see figure 4.13). This may be attributed to the collapse of the stabilising layer no longer preventing mutual attraction of particles. Poly(VBP)-graft-PS stabilisers did not produce stable dispersions of PMMA in cyclohexane. G14C (ASB 0.77:1) produced highly bridged particles under the TEM. The dispersion was observed to be
thixiotropic setting to a solid on standing but reverting to a fluid upon shaking. It is proposed that only weak anchoring occurs between the dispersed phase particle and the poly(VBP) backbone which may be due to incompatibility of PMMA with the backbone. It has been proposed that a minimum anchor molar mass is required for effective anchoring and that the poly(VBP) backbone is not of a sufficient length. Figure 5.9 shows the variation of particle size with ASB for the G12 series of stabilisers. The particle size is directly affected by the copolymer composition. Taylor and Dawkins\(^{16}\) showed that for PDMS-b-PS copolymers that the length of the PDMS block determined the particle size. The higher the molar mass of the PDMS block, the smaller the particles produced. This occurs because the longer siloxane chains are capable of stabilising larger surface areas than the shorter siloxane blocks. Fewer stabiliser molecules are required per molecule therefore producing smaller particles. In the present work, the length of the stabilising grafts is kept constant but the total number per stabiliser molecule is increased. Increasing the number of grafts shortens the copolymer backbone (see section 5.4.1). Surface coverage data showed that the area stabilised per graft decreased with increasing number of grafts per copolymer molecule (see figure 5.10). Therefore, increasing concentrations of stabiliser are required when the number of grafts per copolymer increases in order to produce the same size particles. For graft copolymers, the molar mass of the backbone segments determines the size of polymer particles (see figure 5.11), if the graft frequency and length can provide an effective steric barrier. Further surface coverage data (see table 5.11) for the area stabilised per graft copolymer chain shows that no change in the area stabilised is observed for poly(2-VP)-graft-PS. Poly(4-VP)-graft-PS copolymers stabilise a larger area than the G12 series of copolymers. This difference in the area stabilised is due to the molar masses for the two series of copolymers. The area stabilised is related to the unperturbed dimensions for the copolymers as shown in table
Figure 5.9

Variation of particle size with ASB for Poly(2-VP)-Graft-PS on PMMA in cyclohexane.
VARIATION OF AREA STABILISED PER GRAFT AND DISTANCE WITH ASB FOR POLY(2-VP)-GRAFT-PS ON PMMA/CYCLOHEXANE

- Area Stabilised
- Distance between Grafts
VARIATION OF PARTICLE SIZE WITH BACKBONE MOLAR MASS FOR POLY(2-VP)-GRAFT-PS ON PMMA/CYCLOHEXANE
### TABLE 5.11
SURFACE COVERAGE DATA FOR PMMA DISPERSIONS

<table>
<thead>
<tr>
<th>Graft</th>
<th>Area (nm²)</th>
<th>Stabilised</th>
<th>$d$ (nm)</th>
<th>$M_n$ (kg.mol⁻¹)</th>
<th>$&lt;r_0^2&gt;^{1/2}$ (nm)</th>
<th>$&lt;s^2&gt;^{1/2}$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>G12B</td>
<td>7.3</td>
<td>2.9</td>
<td>27.1</td>
<td>11.0</td>
<td>4.5</td>
<td></td>
</tr>
<tr>
<td>G12C</td>
<td>8.5</td>
<td>3.1</td>
<td>31.0</td>
<td>11.8</td>
<td>4.8</td>
<td></td>
</tr>
<tr>
<td>G12D</td>
<td>7.4</td>
<td>2.9</td>
<td>29.5</td>
<td>11.5</td>
<td>4.7</td>
<td></td>
</tr>
<tr>
<td>G11D</td>
<td>10.3</td>
<td>3.5</td>
<td>41.9</td>
<td>13.7</td>
<td>5.6</td>
<td></td>
</tr>
</tbody>
</table>

NB: area stabilised per copolymer chain

$d = \text{distance between copolymer chains}$

$molar masses determined by membrane osmometry$
5.11A. Barrett⁴ has shown that PMMA-graft-PHSA copolymers with grafts of \( M_n = 1.5 \text{ kg.mol}^{-1} \) provided an effective steric barrier. Previous work in this laboratory¹⁸ has shown that grafts of poly(ethylhexylacrylate) with \( M_n = 1.5 \text{ kg.mol}^{-1} \) did not prevent aggregation of particles, although if \( M_n = 3.0 \text{ kg.mol}^{-1} \) then stable dispersions could be produced. This could be explained in terms of the difference in end-to-end distance for the two polymers.

The difference in behaviour between Poly(2-VP)-graft-PS and poly(4-VP)-graft-PS stabilisers is complex. The two types of graft copolymer have similar ASB values and therefore are predicted to behave in a similar way (their micellar core sizes are similar). The major difference in copolymer structure is the polarity of the copolymer backbone. Poly(4-vinylpyridine) has a higher solubility parameter compared to poly(2-VP).

Therefore, the equilibrium of free graft copolymer to micelles is lower because the energy required to break up the micelles will be larger. GI1B and GI1C are too highly associated to allow graft copolymer molecules to break free and associate with the precipitating polymer chains. The association of the micelles will become weaker as the amount of insoluble component decreases. Therefore, the micellar dispersion of GI1D can dissociate at the polymerisation temperature.

(b) Effect of Stabiliser Concentration

This was investigated using GI1D and GI2D graft copolymers as stabilisers using a one shot polymerisation method. Figure 5.12 shows the variation of average particle size of dispersions prepared in the presence of differing concentrations of the two stabilisers. At all concentrations of stabiliser spherical particles with a narrow particle size range and distribution were produced. Increasing stabiliser concentration produces smaller particles, as predicted by nucleation theories. The number of nuclei produced increases with increasing stabiliser concentration. Barrett⁴ suggested the following relationship
FIGURE 5.12

VARIATION OF PARTICLE DIAMETER WITH [STABILISER]
FOR PMMA/CYCLOHEXANE

Poly (2-VP)-graft-PS
Poly (4-VP)-graft-PS
in which \( D \) is the particle diameter and \( c \) is the concentration of stabiliser. \( x \) the concentration coefficient is the slope determined by a double logarithmic plot (see figure 5.13). Table 5.12 lists the concentration coefficients determined in the present work and by previous workers\(^4,6,7,19,21\). The concentration coefficients for graft copolymers all have approximately the same value of 0.6 while, diblock copolymers are nearer 0.8-0.9.

Dispersion polymerisations of MMA were usually performed in the presence of about 5\% stabiliser in solution. It should be noted that despite this relatively high concentration, only up to 60\% of the copolymer was actually incorporated onto the PMMA particles. With highly grafted stabilisers the amount was generally nearer 20\% of copolymer.

(c) Effect of Monomer Concentration

This was investigated using G12D as a stabiliser with a one shot polymerisation method. Figure 5.14 shows the variation of the average particle size of dispersions in the presence of differing monomer concentrations. Spherical particles with a narrow size distribution were produced. The polydispersity of the particles increased with increasing monomer concentration in the polymerisation. As the monomer concentration increases, larger particles are produced. This is in agreement with theories for particle formation. Since MMA is a solvent for PMMA, it is expected that the threshold molar mass for precipitation of the growing chains will be dependent on the monomer concentration in the dispersion medium (assuming all other parameters are constant). Therefore, higher monomer concentrations will produce higher threshold molar masses before particle nucleation. Thus, the size of the initial nuclei formed is larger being related to the solvency of the dispersion medium. However, the efficiency of the stabiliser may be altered by the presence of large amounts of monomer in
FIGURE 5.13

PLOT OF log(PARTICLE DIAMETER) VS log(STABILISER) FOR PMMA/CYCLOHEXANE

\[ y = 0.184 - 0.653x \quad r^2 = 0.944 \]
\[ y = 0.065 - 0.640x \quad r^2 = 1.000 \]

- Poly (2-VP)-graft-PS
- Poly (4-VP)-graft-PS
<table>
<thead>
<tr>
<th>Stabiliser</th>
<th>x</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>poly(4-VP)-graft-PS</td>
<td>0.64</td>
<td>This work</td>
</tr>
<tr>
<td>poly(2-VP)-graft-PS</td>
<td>0.65</td>
<td>This work</td>
</tr>
<tr>
<td>PDMS-block-PS</td>
<td>0.77</td>
<td>7</td>
</tr>
<tr>
<td>PS-block-poly(ethylene-co-propylene)</td>
<td>0.98</td>
<td>6</td>
</tr>
<tr>
<td>PS-graft-poly(ethylhexylacrylate)</td>
<td>0.63</td>
<td>18</td>
</tr>
<tr>
<td>polyisoprene-block-PS-block-polyisoprene</td>
<td>0.36-0.46</td>
<td>211</td>
</tr>
<tr>
<td>poly(12-hydroxystearic acid) grafts and various backbones</td>
<td>0.5-0.6</td>
<td>4</td>
</tr>
</tbody>
</table>
FIGURE 5.14

VARIATION OF PARTICLE DIAMETER WITH [MOMONER]

FOR POLY(2-VF)-GRAFT-PS STABILISED PMMA
the reaction medium, since the monomer acts as a solvent for the stabiliser anchor block. Consequently, there is less of a driving force for adsorption than when the reaction medium is a relatively poor solvent for the anchor block. This observation implies that coalescence of the newly formed nuclei could be an important mechanism in the formation of larger particles. Antl et al.\textsuperscript{213} have reported similar behaviour of MMA in n-hexane with particle size varying from 80nm for monomer concentrations of less than 8.5%. At concentrations of 35 to 50%, the particle size varied from 0.18 to 2.6\,\mu m. Between 8.5 and 35\% monomer concentration unstable dispersions were produced. The addition of a solvent for the dispersed polymer particle will have a similar effect to increasing the monomer concentration. Croucher et al.\textsuperscript{210} added carbon tetrachloride to the dispersion medium and observed that the particle size varied in a similar manner to the work by Antl.

(d) Effect of Initiator Concentration

This was investigated using G12D as a stabiliser in a one shot polymerisation method. Figure 5.15 shows the variation of particle size with initiator concentration. Spherical particles with a narrow size distribution were produced. The initiator concentration will affect the number of free radicals generated. This would control the number of nuclei that are formed and consequently effect the final particle size. It is observed that the higher the initiator concentration, the larger the final particle size. No significant increase in polydispersity is observed with increasing initiator concentration. Both the self nucleating and aggregative nucleation mechanisms predict that the number of nuclei is proportional to the rate of radical generation. Therefore, increasing amounts of initiator produce more oligomers predicting, more particles. The implications of increasing particle size with higher initiator concentration will be discussed in the next section.
FIGURE 5.15

VARIATION OF PARTICLE DIAMETER WITH [INITIATOR] FOR POLY(4-VP)-GRAFT-PS STABILISED PMMA

[Graph showing the variation of particle diameter with [initiator] by wt%]
(e) Surface Morphology

An SEM micrograph of a PMMA dispersion is shown in figure 4.14. The particles stabilised with G11D and G12D showed a non-smooth lumpy surface. This was more evident on the larger particles (i.e. low stabiliser or high monomer concentration experiments). TEM micrographs of particles stabilised with G12B and G12C before purification showed the presence of 40-50 nm diameter particles as well as the larger 0.2-0.3 um particles. PMMA has a Tg of 377K which is well above the reaction temperature of 343K, although the Tg of PMMA in the reaction media will be lowered by the presence of plasticising agents such as free monomer and any diluent effect. It is believed that the lumpy surface morphology may be attributable to coalescence of primary particles after nucleation. The lumpy morphology will be observed if the monomer swollen PMMA in the particle is below its Tg. It can be inferred that the amount of monomer available to depress the Tg of the PMMA must be low otherwise a smooth morphology would be observed. It is probable that coalescence occurs at a late stage in the polymerisation. If a large number of very small particles are produced at the nucleation stage, large amounts of stabiliser are required to stabilise the surface area of the particles. It could be conceivable that because of the partitioning of the graft copolymer between micelles and adsorbed stabiliser on the particle surface, there is insufficient stabiliser to cover the surface area of all the particles. Therefore, primary particles will coalesce because of the lack of an effective steric barrier. The graft copolymer stabiliser will be in equilibrium at the start of the polymerisation as in figure 2.8 between unassociated graft copolymer and graft copolymer micelles. The monomer will influence the behaviour of the graft copolymer in the dispersion medium by solvating the micelle core. This will lead to more free unassociated graft copolymer present at the initial stages of polymerisation. As the polymerisation proceeds, the equilibrium is shifted by free graft copolymer
molecules being adsorbed by the growing oligomer chains and eventually being adsorbed onto the particle surface after nucleation. The amount of monomer available to solvate the micelle core drops as it is consumed to form polymer thus shifting the equilibrium towards graft copolymer micelles, and therefore decreasing the amount of graft copolymer available for adsorption onto the growing primary particles. This model predicts that the more polar the micelle core (i.e. the greater the free energy of association), the greater the chance of coalescence occurring. For stabilisers G11B and G11C stable dispersions could not be achieved, although flocculation only occurred after 5 and 40 minutes respectively. This could be attributed to the primary particles being stable but upon growth not enough stabiliser was available for adsorption thus allowing coalescence and eventually flocculation. The rate of new surface area created \( dA \), is given by

\[
dA = \frac{3 \, dV}{r}
\]

where \( dV \) is the rate of new volume created and \( r \) is the particle radius. The rate of new surface area created decreases with increasing \( r \). Therefore, the smaller the primary particles, the faster the rate of surface area created and therefore, higher rates of adsorption of stabiliser are required. Calculation with 5\% by wt. stabiliser (G12C), 20\% by wt. monomer in a dispersion polymerisation with a 100\% efficient anchoring mechanism will result in particles having a 76 nm diameter, if all the monomer is consumed. Clearly this is the smallest particle size that can be attained using G12C at 5\% dispersant level. If the initial particle size is smaller, all the stabiliser will be consumed earlier in the dispersion, and any new surface area created will not be covered by stabiliser and coalescence will occur as no steric barrier is present. Barrett et al\(^4\) has commented on the coalescence of PMMA with irreversibly anchored stabilisers. It was observed that ultra-fine polymer particles appeared to be destabilised during particle growth, but coalescence occurred to form larger
spherical particles. Analysis of the data presented by Antl et al.\textsuperscript{212} showing the variation of the monomer concentration with particle size. An unstable region in which particles were initially stable but subsequently flocculated between 8.5 and 35% monomer concentration was observed. Below 8.5% monomer concentration particles of 80nm were produced. Above 35% monomer concentration, the particle size varied between .18 to 2.6 um. It can be concluded that at low monomer concentrations, the primary particles are very small, requiring large amounts of stabiliser with respect to monomer. At intermediate monomer concentrations, as the particles grow to even larger sizes, not enough free stabiliser is available for adsorption onto the particle surface thus leading to coalescence and eventually floculation. At higher monomer concentrations, the solvency of the dispersion medium is higher, and therefore, the threshold molar mass for nucleation to take place is also higher. The number of nuclei produced will be lower probably occurring by an aggregative nucleation, thus producing primary particles of a larger size. Therefore, the rate of stabiliser adsorption required to stabilise the particle surface is lower as it follows equation 5.10.

The effect of initiator concentration showed that the predicted number of nuclei should increase with higher initiator concentration. If this is assumed to be correct with an increasing number of small primary particles produced, the overall rate of surface area created during particle growth will increase. Thus, the amount of coalescence will also increase leading to a smaller number of larger particles.

(f) Surface Coverage

Surface coverage data for PMMA particles are shown in table 5.10. Figure 5.16 shows the variation of percentage of graft copolymer on the particle to the particle diameter. On the basis of graft copolymer to monomer in the original dispersions, only up to 55% of the stabiliser available was incorporated. Higher concentrations of stabiliser were required
VARIATION OF %COPOLYMER FOUND ON PMMA WITH PARTICLE DIAMETER

FIGURE 5.16

poly (2-VP)-graft-PS
poly (4-VP)-graft-PS
than necessary since the adsorption mechanism is not 100% efficient and may be due to the different chemical nature of the anchor block to the PMMA in the particle. The surface area A occupied by each stabilising PS chain was then calculated from the graft copolymer content of the particles and the average particle size Dn. It was assumed that the stabilisers only occupied the surfaces of the particles, and the anchor block did not extend significantly into the dispersion medium and that the PS chain was terminally anchored to the particle surface. It was also assumed that no overlap of stabiliser anchor blocks occurred. By further assuming that each PS chain was anchored at the centre of a regular hexagon of area A, the mean separation distance d between adjacent grafts was calculated.

The results suggest that for the same graft copolymer the area stabilised and the distance between grafts did not alter with particle size. It was observed that the area stabilised did vary with graft copolymer composition. As the graft length of the stabiliser was kept constant, it can be inferred that the copolymer backbone controlled the area stabilised per graft. Figure 5.17 shows the variation of the distance between grafts and the stabiliser anchor segment molar mass between grafts. Figure 5.18 shows the variation of the distance between grafts and the radius of gyration of the backbone segment between grafts. This disagrees with Dawkins and Taylor\textsuperscript{16} for PMMA dispersions stabilised with PS-b-PDMS copolymer. They found that the length of the stabilising block (PDMS) controlled the area stabilised and not the length of the anchor block. Taylor found for PDMS (M\textsubscript{n}=3.2 kg.mol\textsuperscript{-1}) that A = 6.4 nm\textsuperscript{2} and d = 2.7 nm. In the present work, A = 1.0 - 2.5 nm\textsuperscript{2} and d = 1.05 - 1.71 nm. Slark\textsuperscript{18} found similar values for PMMA dispersions stabilised with PS-graft-PEHA copolymers of a similar graft molar mass to the PS grafts in the present work. Barrett et al\textsuperscript{4} calculated A = 3.0 nm\textsuperscript{2} and d = 1.7 nm for PMMA-graft-PHSA copolymer with graft of M\textsubscript{n}=1.5 kg.mol\textsuperscript{-1}. 

-110-
FIGURE 5.17

VARIATION OF MEAN PS GRAFT SPACING (d) WITH MOLAR MASS OF BACKBONE SEGMENT

\[ d \text{ (nm)} \]

\[ M_n \text{ (segment)} \]
FIGURE 5.18

PLOT OF MEAN PS GRAFT SPACING (d) VS RG OF POLY(2-VP) BACKBONE SEGMENT

Rg (nm) of M(segment)

0.0 0.3 0.5 0.8 1.0 1.3 1.5 1.8 2.0

0.0 0.3 0.5 0.8 1.0 1.3 1.5 1.8 2.0
Comparison of the area stabilised for micellar dispersions in toluene and cyclohexane (see table 5.5) for G11 and G12 graft copolymers shows a direct correlation. The distance between adjacent grafts are very similar for PMMA and micellar dispersions. Therefore, it can be inferred that the conformation of the backbone is similar in both micelles and PMMA particles. Table 5.13 shows the predicted chain lengths of Poly(4-VP) and Poly(2-VP) of various molar masses in different conformations.

It can be concluded that at high graft frequencies the distance between grafts is controlled by the graft copolymer architecture. At low graft frequencies, the distance between grafts increases and stable dispersions can be achieved up to the maximum value predicted by similar block copolymers. If the distance between grafts exceeds this critical value, then the copolymer cannot provide an effective steric barrier. Block copolymers can arrange themselves into a far larger number of configurations on the particle surface (see figure 5.19) than graft copolymers. Therefore, a block copolymer can spread the stabilising chains across the surface at the optimum distance apart. This optimum distance is balanced by the repulsive energies between the stabilising chains in solution and the driving force to provide an effective steric barrier. With graft copolymers, the optimum distance cannot be achieved because the grafts are attached to the copolymer backbone and are a fixed distance apart. Therefore, there is an excess repulsive energy between the stabilising grafts in solution compared to block copolymers, this may lead to chain extension of the PS grafts (see section 5.7.2). In conclusion, the free energy for steric stabilisation is reduced for graft copolymer stabilised dispersions compared to block copolymers assuming that the energy of interaction between the anchor components is similar.
TABLE 5.13
DIMENSIONS OF VARIOUS CHAINS IN DIFFERENT CONFORMATIONS

<table>
<thead>
<tr>
<th>Molar Mass Kg.mol(^{-1})</th>
<th>(\langle r_0^2 \rangle^{\frac{1}{2}})</th>
<th>(\langle s^2 \rangle^{\frac{1}{2}})</th>
<th>(L_{\text{max}})</th>
<th>(\langle V_s^2 \rangle^{\frac{1}{2}})</th>
</tr>
</thead>
<tbody>
<tr>
<td>PS</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3.2</td>
<td>3.79</td>
<td>1.55</td>
<td>6.82</td>
<td>8.08</td>
</tr>
<tr>
<td>Poly(4-VP)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.6</td>
<td>2.84</td>
<td>1.16</td>
<td>3.33</td>
<td>5.23</td>
</tr>
<tr>
<td>3.5</td>
<td>4.20</td>
<td>1.71</td>
<td>7.29</td>
<td>9.37</td>
</tr>
<tr>
<td>5.3</td>
<td>5.14</td>
<td>2.10</td>
<td>10.7</td>
<td>12.75</td>
</tr>
<tr>
<td>Poly(2-VP)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.4</td>
<td>2.47</td>
<td>1.01</td>
<td>2.92</td>
<td>4.25</td>
</tr>
<tr>
<td>2.5</td>
<td>3.27</td>
<td>1.33</td>
<td>5.10</td>
<td>6.42</td>
</tr>
<tr>
<td>4.2</td>
<td>4.28</td>
<td>1.75</td>
<td>8.75</td>
<td>9.70</td>
</tr>
</tbody>
</table>

NB
all dimensions in nm
FIGURE 5.19
CONFIGURATIONS OF A DIBLOCK COPOLYMER AND A GRAFT COPOLYMER ON A PARTICLE SURFACE

diblock copolymer

graft copolymer
Dispersion Stability

PMMA dispersions were all stable over a long period of time. Sedimentation took place over a period of days to weeks depending on the particle size and the storage temperature. Redispersion of the particles was easily performed by shaking. This long term stability suggests no desorption of the stabiliser, and stability under ultrasonic vibration showed that the anchoring mechanism was not weak.

PMMA has been shown to be compatible with poly(4-VP) by DMTA. It is therefore postulated that the anchor block of poly(4-VP) or poly(2-VP) is expected to be an unperturbed random free coil conformation. The anchoring block will be in loops extending into the particle.

Preliminary flocculation studies were performed on PMMA particles. It is well documented that cyclohexane is a theta solvent for PS at 307K. Under theta conditions, the repulsive and attractive energies are equal. In the absence of a repulsive energy, the particles would flocculate. It has been previously reported that flocculation does indeed take place at or near the theta point for a wide range of different dispersions with different stabilising moieties. In the present work, flocculation could be induced by the addition of a non-solvent for the stabilising chains, such as methanol. Cooling of the dispersions below 307K failed to induce flocculation, even at 283K no flocculation was observed to occur. These findings disagree with the published work for high molar mass stabilising chains. Vincent et al have observed for aqueous dispersions of PS stabilised with a low molar mass PEO stabiliser that the critical flocculation temperature is not related to the theta temperature. Further work is required to resolve the disparities observed in the present work with the observations for high molar mass stabilisers.
5.7.2 Dispersion Polymerisation of Vinylpyridine

The results of dispersion polymerisations of vinylpyridine were shown in table 4.14. The experimental procedure in section 3.8.5 was used. Stable dispersions were achieved using G11 and G12 series of graft copolymers in cyclohexane and toluene. Poly(2-vinylpyridine) is soluble in toluene and therefore it is not possible to produce particles with this system. No previous studies of the dispersion polymerisation of poly(vinylpyridine) have been reported.

No assessment of the rate of dispersion polymerisation was made, but it is assumed that a similar behaviour to MMA is observed. Near complete conversion was achieved after 22 hours. The solubility of poly(4-vinylpyridine) in toluene and cyclohexane is almost negligible; poly(2-vinylpyridine) is not soluble in cyclohexane. Swelling of the particles was not considered a problem compared to PS in aliphatic hydrocarbons because of the increased polarity of poly(VP).

Electron microscopy has shown that the particles produced were spherical and of a reasonably narrow size distribution (as seen in figure 4.15 & 4.16). Only the one shot polymerisation technique was used to prepare dispersions. Nucleation of particles was thought to occur only at the beginning of the polymerisation because of the narrow size distribution of the particles.

(a) Effect of Graft Copolymer Composition

In toluene both the G11 and G12 stabilisers produced stable dispersions of poly(4-vinylpyridine) (see Table 4.14). G11A and G12A did not produce stable micellar dispersions and therefore were not thought to be ideal stabilisers for particles. No correlation was found between particle size and copolymer composition for the G11 series. The average diameter was approximately 60nm. The electron micrographs showed that at low graft frequencies the particles were more aspherical and some
bridging occurred. The bridging may be due to the collapse of the stabilising barrier when the dispersion medium is removed.

Stabilisers with a poly(2-VP) backbone produced larger particles than similar copolymers containing poly(4-VP) in toluene. Since poly(2-VP)-graft-PS is completely soluble in toluene, the interaction of stabiliser with growing oligomer chains before nucleation will be less. Because the driving force for the adsorption of stabiliser (the insolubility of the anchor block in the dispersion medium) is not present. Smaller number of larger nuclei produce larger particles.

(b) Effect of Diluent and Monomer

Identical dispersion polymerisations were performed in cyclohexane and toluene. For the G11 series of stabilisers adsorbed onto Poly(4-VP) in cyclohexane, flocculation was found to occur after polymerisation had started; typically after 1 hour and 18 hours for G11B and G11D respectively. Therefore, nucleation and growth of particles did take place until a critical point was reached and flocculation occurred. It is predicted that in cyclohexane the poly(4-VP) particles will be smaller but larger in number compared to toluene and therefore require a higher percentage of stabiliser per particle. As discussed in section 5.7.1, the equilibrium between free graft copolymer and micelles will alter with consumption of monomer. The association of micelles in cyclohexane is higher than in toluene; therefore, less free graft copolymer is available for adsorption onto the growing particle surface. Agglomeration and coalescence occur producing larger particles. In the present case, flocculation occurs which is the extreme case when insufficient stabiliser is available. The difference in time for flocculation to occur may be due to the difference in association between G11B and G11D. As the stabilising graft content increases, the anchor component decreases, thus having
a lower energy of association and thus shifting the equilibrium towards free graft copolymer.

Stabilisers containing poly(2-VP) backbones were found to be effective in both cyclohexane and toluene (see figure 4.16). Particles of Poly(4-VP) were smaller in cyclohexane than in toluene; this is to be expected from nucleation theory, as the threshold molar mass for nucleation will be lower in cyclohexane, thus producing a larger number of smaller nuclei.

Dispersions of poly(2-VP) and poly(4-VP) under the same conditions in cyclohexane using G12C as a stabiliser showed a difference in particle size. Dispersions of poly(2-VP) were larger than poly(4-VP). The threshold molar mass of poly(2-VP) in cyclohexane is higher than poly(4-VP) because of the difference in solubility parameter related to the relative polarity of the polymers. Lower threshold molar mass will produce smaller nuclei. In both dispersions before purification, smaller particles of diameter <50 nm are seen. These particles (poly(2-VP) = 40-50 nm, poly(4-VP) = 25-35 nm) may be primary particles that have not coalesced or due to secondary nucleation. If secondary nucleation was occurring a rapid change of solvency of the dispersion medium would be needed in order to produce a second crop of nuclei of a uniform size; this is thought unlikely. As stated previously for PMMA dispersions, controlled agglomeration and coalescence may occur if insufficient stabiliser is present.

(c) Effect of Stabiliser Concentration

The level of stabiliser in the dispersion polymerisation of poly(4-VP) was varied. Lower concentrations of stabiliser produced larger particles in accordance with the predicted theory. At 0.61% by wt stabiliser, some precipitated polymer was formed as well as stable dispersed poly(4-VP) particles. The anchoring efficiency can be estimated approximately by calculating the minimum particle size at a known stabiliser concentration. As stated in section 5.7.1, the minimum particle
size at 5% by wt. stabiliser (G11D) is 62nm. Therefore, it is assumed that the anchoring efficiency is nearly 100% within experimental error, as particles of 66nm were produced. For particles at 1% by wt. stabiliser, the predicted minimum size is 254 nm. Particles of 120nm were actually produced which are smaller than the predicted size. Therefore, there must not be 100% surface coverage. Higher anchoring efficiencies are to be expected for poly(4-VP)-graft-PS stabilisers with poly(4-VP) particles as the anchor block and the core of the particle are the same polymer.

(d) Dispersion Stability

Dispersions were found to be stable over very long periods of time (in excess of six months) with no sedimentation of particles being observed. Therefore, no desorption of stabiliser occurred. This stability is to be expected because of the small size of the particles and the anchor block of the stabiliser would be incorporated into the particle matrix, thus anchoring the stabilising block (grafts) firmly to the particle. Ultrasonic vibration did not affect dispersion stability. The conformation of the anchor block chains in the particle is predicted to be similar to that of the bulk polymer. Flory predicted that these would be the unperturbed random coil dimensions, this was later proved experimentally.

Flocculation of the dispersions could be achieved by the addition of a nonsolvent (acetone) for the stabilising block. This infers that steric stabilisation is the predominant mechanism for dispersion stability. No controlled flocculation studies were performed to determine whether flocculation occurred close to the theta point for the stabilising chains.

SAXS was performed on FRD36, 37, and 38, to determine the core size of the particle and the fringe thickness. Results were presented in table 4.20. The core size determined by SAXS gives a value for $D_z$. Comparison with the data obtained by TEM
shows good agreement. The core diameter determined by SAXS was slightly larger than by TEM. This may be explained either by shrinkage of the particle upon removal of the dispersion medium or the errors involved determining the core diameter. SAXS errors increase as the core diameter increases. Because scattering from the particle appears at very low angles. The fitting of a Fourier series to the smeared intensities induces more errors as the scattering curve becomes narrower. One of the assumptions made in fitting the fourier series is the gradient at 0 degrees is zero which becomes increasingly difficult. The Guinier plot determines the radius of gyration of the core of the particle from the \((-\text{gradient})^{0.5}\); as the gradient becomes larger, the errors increase. The determination of the fringe thickness gives an indication of the thickness of the stabilising layer. The stabilising layer is composed of PS grafts terminally linked to the particle surface extending into the dispersion medium. The dimensions of different conformations of PS grafts have already been shown in table 5.8. The results (see table 4.20) show that the conformation of the PS grafts changes with graft frequency, i.e. chain extension occurs when grafts are closer together. For FRD36 the conformation of the PS graft is similar to an unperturbed chain of the same molar mass. The distance between grafts for FRD38 (G11D) is close to the Van-der-Waals dimensions for two adjoining PS graft units (considering the presence of the diphenylethylene unit close to the branching site). In order to minimise this energy of repulsion, some chain extension will take place. Previous workers\(^{217,218}\) have observed for diblock copolymer stabilised particles some chain extension. Taylor and Dawkins\(^{217}\) determined using hydrodynamic methods the surface layer thickness of PDMS chains, they observed a conformation between a random coil and an extended conformation. Shakir and Dawkins\(^{218}\) for S-EP block copolymer stabilised particles determined the surface layer thickness using hydrodynamic methods and observed a slightly extended conformation compared to a random coil in both good and theta solvents. The
determination of the surface layer thickness can be achieved using alternative techniques such as small-angle neutron scattering, photon correlation spectroscopy and attenuated total reflection. SAXS determines the fringe thickness as a function of electron density, errors may arise compared to hydrodynamic methods since a sharp change in electron density will not occur between the fringe and the solvent. Other errors incurred in the SAXS calculations have been discussed in section 5.5.1 including the low number of counts recorded at high angles. The validity of the various electron density profile models have been outlined earlier and the range over which errors are considered to be minimal. The empirical solution relies on an approximation of a Maclaurin series which may be open to doubt. Even if there is some basis for doubt in the absolute values obtained by SAXS the differences between the values is still significant.

Chain extension of the grafts might be expected, since it represents a balance between excluded volume effects extending the molecule to increase polymer-solvent interactions, and the loss of entropy associated with extending the molecule. Whilst such extension occurs in solution, the elongation is even greater for a terminally adsorbed molecule, owing to the anisotropic situation. The molecule cannot penetrate the surface, and is severely restricted in the penetration of neighboring volumes but is free to extend in a perpendicular plane to the surface. De Gennes predicted using the concept of scaling that chain extension of terminally adsorbed polymers will be in an extended conformation similar to a brush. The mean field theory has also been applied to a similar situation and comparable results are predicted.

5.7.3 Dispersion Polymerisation of Styrene

Dispersions of PS were prepared free radically as described in section 3.8.4, and the results are recorded in table 4.15. The dispersion polymerisation of styrene has been extensively reported in the literature using a wide range of different
Stabilisers. Stabilisation of PS dispersions by adsorbed graft copolymer in an inverted conformation is a novel system. Studies were also performed using homopolymer backbones as stabilisers. The calculation of the average area stabilised per chain for these systems is given in table 5.14.

The rate of polymerisation was not studied, but all experiments were taken to high conversions. Typically, 80+% conversions were achieved after 22 hours. Taylor has determined the rate of dispersion polymerisation of PS in heptane using block copolymer stabilisers. Only 50% conversions were obtained within 50 hours. Particle size is dependent on a number of variables including conversion. Therefore, all experiments were taken to similar conversions.

The solubility of PS in methanol is almost negligible. Swelling of the particles was, therefore, not considered. Elasser and Vanderhoff observed that the plot of monomer conversion with time had a sigmoidal form, similar to MMA dispersion polymerisations. A more pronounced gel effect was observed when the polarity of the dispersion medium was increased by adding water. The molar masses of PS dispersions are shown in table 4.19. Conventional solution polymerisation of PS under similar conditions predicts a number average molar mass of $5 \times 10^4 \text{g.mol}^{-1}$. Generally molar masses were $1.2 \times 10^5 \text{g.mol}^{-1}$ for PS dispersions indicating that the gel effect was occurring.

Electron microscopy has shown that the particles of PS produced were spherical and of a variable particle size distribution. Significant improvement in distribution was observed by using seed/feed techniques instead of one shot methods for some experiments, notable when homopolymers were used as stabilisers. The use of a seed stage in polymerisations did produce significantly smaller particles, which agrees with previous work done at loughborough. The solvency of the dispersion medium is also likely to modify the behaviour of the stabiliser and the critical threshold molar mass for particle distribution.
<table>
<thead>
<tr>
<th>Code</th>
<th>Stabiliser</th>
<th>$D_n/\mu m$</th>
<th>Content (%w/w)</th>
<th>Stabilised (nm)</th>
<th>$d$ (nm)</th>
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<tr>
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<td>P(4VP)A</td>
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<td>.194</td>
<td>258</td>
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<td>P(4VP)A</td>
<td>.815</td>
<td>.087</td>
<td>473</td>
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<tr>
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<td>P(4VP)A</td>
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<td>.145</td>
<td>244</td>
<td>16.8</td>
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<td>P(4VP)A</td>
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<td>.038</td>
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<tr>
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<td>P(4VP)B</td>
<td>.83</td>
<td>.043</td>
<td>698</td>
<td>28.4</td>
</tr>
<tr>
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<td>P(4VP)C</td>
<td>.77</td>
<td>.063</td>
<td>1350</td>
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</table>
nucleation. Higher solvency (i.e. larger amounts of styrene monomer in the seed stage) will reduce the tendency for the stabiliser to associate with growing polymer chains during particle formation in addition to impairing the efficiency of the anchoring mechanism of particles already formed. A number of workers have observed in methanol based systems a linear relationship between monomer concentration and particle size, using one shot polymerisations. This simple relationship does not exist for PMMA dispersions in aliphatic hydrocarbons.

(a) Effect of Stabiliser Composition on Particle Size

Stabiliser structure was found to be an important factor in dispersion polymerisation (see table 4.15). For poly(2-VP)-graft-PS copolymers stable dispersions were produced with the exception of G12D (ASB = 0.50:1), which phase separated in methanol. Poly(4-VP)-graft-PS copolymers were also successful with only G11D (ASB = 0.45:1) not producing stable dispersions. The homopolymers all produced stable dispersions although the final particle size produced was considerably larger than when graft copolymers were used. No significant variation of particle size with a copolymer structure was found, although slightly smaller particles were produced with higher graft copolymers. In the present work, the length of the anchoring grafts is kept constant but the total number per stabiliser molecule is increased. Increasing the number of grafts shortens the copolymer backbone (see section 5.4.1). Therefore, the effective area that each backbone can stabilise will decrease. Consequently, increasing concentrations of stabiliser are required when the number of grafts per copolymer increases in order to produce the same particle size.

The difference in particle size between poly(2-VP)-graft-PS and poly(4-VP)-graft-PS stabilised particles is more complex. Similar trends are observed when poly(2-VP) and poly(4-VP) are used as stabilisers. The two types of graft copolymer have similar ASB values and, therefore, are predicted to behave in a similar way. The major difference in copolymer structure is the
polarity of the copolymer backbone. Poly(4-vinylpyridine) has a higher solubility parameter compared to poly(2-VP), and therefore methanol is a 'better' solvent for poly(4-VP). The chain conformation of poly(4-VP) is predicted to be in a more extended state than poly(2-VP). Therefore, a poly(4-VP) molecule of the same molar mass as poly(2-VP) will stabilise a larger area, thus forming smaller particles.

The large difference in particle size using homopolymers as stabilisers compared to graft copolymers is related to the difference in behaviour of the polymers in solution. At the onset of polymerisation, the growing oligomer chains will associate with free graft copolymer molecules in order to minimise the free energy of the polymer in the dispersion medium, once the critical threshold molar mass is reached and nucleation occurs, the graft copolymer is adsorbed onto the particle surface. When the dispersion polymerisation is carried out with homopolymer stabilisers, the driving force to associate the growing oligomer chains with a stabiliser molecule is not present to the same degree. Nucleation processes are modified by the presence of stabiliser. As stated in section 2.2.4, a larger number of smaller nuclei are predicted. Therefore, without the same level of association of the stabiliser, the nuclei are larger. Other processes may be involved in determining the use of homopolymers as stabilisers. It has been suggested\textsuperscript{224,225} that chain transfer reactions to homopolymer to produce graft copolymers occurs first. These can then associate much more effectively with the growing oligomer chains. Chain transfer constants are shown in table 5.15 for styrene polymerisations in the presence of various polymers.

Different molar masses of poly(4-VP) were used as stabilisers. No variation in particle size was observed as a function of molar mass. It would be interesting to use an ultra-high molar mass poly(4-VP) as a stabiliser to study any possible bridging effects. Corner\textsuperscript{226} used poly(acrylic acid) as
<table>
<thead>
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<th>Polymer</th>
<th>$C_p \times 10^4$</th>
<th>$T(°C)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>poly(methyl methacrylate)</td>
<td>16.4</td>
<td>60</td>
</tr>
<tr>
<td>polypropylene</td>
<td>0.025</td>
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<td>polystyrene</td>
<td>1.9</td>
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<tr>
<td>poly(vinyl acetate)</td>
<td>6.6</td>
<td>100</td>
</tr>
<tr>
<td>poly(2-vinyl pyridine)</td>
<td>8-10</td>
<td>50</td>
</tr>
</tbody>
</table>
a stabiliser and found no dependence on molar mass of the stabiliser.

Homopolymers and graft copolymers containing poly(VBP) were not that successful at stabilising PS dispersions. Poly(VBP) homopolymer stabilised PS dispersions were of a wide size distribution and showed some bridging between particles. If the backbone is considered to consist of polystyrene with pendant pyrrolidone units. It is probable that the size of the stabilising loops is small leading to interaction between the dispersed phase PS and the stabilising loop. The poly(VBP)-graft-PS copolymers produced similar size particles as the homopolymer, and only G14A (ASB 5.5:1) produced a stable dispersion.

(b) Effect of Stabiliser Concentration

This was investigated using G11A and poly(4-VP)A graft copolymers as stabilisers using a one shot polymerisation method. Figure 5.20 shows the variation of average particle size of dispersions prepared in the presence of differing concentrations of the two stabilisers. Increasing stabiliser concentration produces smaller particles, as predicted by nucleation theories. The number of nuclei produced increases with increasing stabiliser concentration. Barrett suggested the following relationship

\[ D \propto c^x \]

in which D is the particle diameter and c is the concentration of stabiliser. The concentration coefficient, x can be determined from the slope of a double logarithmic plot (see figure 5.21). It was found that x≈.351 for G11A and .529 for poly(4-VP)A. Corner found that the particle size varied with concentration of stabiliser (polyacrylic acid) passing through a maximum at 4% by wt.

Dispersion polymerisations of styrene were usually performed in the presence of about 5% by wt. stabiliser in solution. It should be noted that despite this relatively high
Figure 5.20

Variation of particle diameter with [stabiliser] for PS stabilised with G11A and Poly(4-VP)A

- Poly(4-VP)-graft-PS (G11A)
- Poly(4-VP)A

[Stabiliser] by %wt.
PLOT OF log(PARTICLE DIAMETER) VS log(STABILISER)

- poly(4-VP)-graft-PS (G11A)
- poly(4-VP)A

$y = 0.171 - 0.530x \quad r^2 = 0.922$

$y = -0.845 - 0.351x \quad r^2 = 0.901$
concentration, only up to 0.25% by wt. of homopolymer was actually incorporated onto the PS particles. No surface coverage data is available for graft copolymer stabilised lattexes, although it is expected nearly all the stabiliser is adsorbed onto the particle surface.

(c) Dispersion Stability

Dispersions were found to be stable over very long periods of time (in excess of six months), with no sedimentation of the smaller particles being observed. Therefore, no desorption of stabiliser occurred. The stability is to be expected for graft copolymer stabilised dispersions as the anchor block of the stabiliser would be incorporated into the particle matrix. Thus anchoring the stabilising block (grafts) firmly to the particle. Ultrasonic vibration did not affect dispersion stability of homopolymer and graft copolymer stabilised dispersions, so both types of stabiliser are firmly anchored. The conformation of the graft copolymer anchor block chains in the particle are predicted to be similar to that of the bulk polymer. Flory\(^{181}\) predicted that these would be the unperturbed random coil dimensions, this was later proved experimentally\(^ {216}\). It is not entirely clear whether grafting of the poly(VP) homopolymers has occurred, although the probability of stabiliser desorption will be reduced if grafting reactions have occurred. Chain transfer constants suggest that grafting may occur.

Flocculation of the dispersions could be achieved by the addition of a nonsolvent (water) for the stabilising block. This infers that steric stabilisation is the predominant mechanism for dispersion stability. No controlled flocculation studies were performed to determine whether flocculation occurred close to the theta point for the stabilising chains.

(d) Surface Coverage

Combining the information on the % stabiliser in the polymer particle (see table 4.18) and the diameter of the particles by
TEM, it was possible to calculate the area stabilised per chain. Quite large errors are involved in determining the stabiliser content as it was present in only very low amounts, and integrations of the $^1$H nmr would be subject to quite large errors. Higher molar mass homopolymers stabilised a larger surface area.

Mean field and scaling concept theories for the physical adsorption of polymers onto surfaces predicts that the layer thickness is determined largely by the tail size\textsuperscript{227}. The loop size increases with increasing chain length but levels off at high values of $x$ (the number of repeat units per chain) where as the average tail length is approximately proportional to the molar mass. The ratio of tail length to chain length depends on solution concentration. In the dispersions made in the present work, the size of loops, tails and trains have been dictated by the graft copolymer structure.
6. CONCLUSIONS

Styryl-terminated polystyrene macromonomers with molar mass of $M_n = 3.0 \text{ kg.mol}^{-1}$ were synthesised by anionic polymerisation using sec-butyl lithium as an initiator. End capping of the polystyryl lithium was performed using vinyl benzyl chloride. Diphenylethylene was added prior to vinyl benzyl chloride to prevent side reactions. These macromonomers were characterised by GPC in THF and $^1H$ nmr. The molar masses of the macromonomers was readily controlled by varying the ratio of the concentration of monomer to initiator. The macromonomers chains were found to be approximately monofunctional, within experimental error.

Poly(4-VP)-graft-PS, poly(2-VP)-graft-PS and poly(VBP)-graft-PS copolymers, with grafts of $M_n = 3.0 \text{ kg.mol}^{-1}$, were synthesised by the free-radical copolymerisation of 4-vinylpyridine, 2-vinylpyridine and N-(vinylbenzyl)pyrrolidone ($M_1$) with the styryl-terminated PS macromonomer ($M_2$), respectively. Conditions were altered so that molar masses of the copolymers were significantly different from the molar masses of the macromonomer. The copolymerisations were performed at different conversions to assess the drift in feed composition with increasing conversion. "Blank" polymerisation experiments with diphenyl-terminated PS showed that the macromonomers were incorporated by the copolymerisation of the terminal unsaturation rather than by transfer reactions involving the PS segments. Purification of the copolymers was achieved removing unreacted comonomer, macromonomer and initiator. GPC showed that the unreacted macromonomers were removed. Characterisation of the copolymers was performed by GPC in DMF, $^1H$ nmr and membrane osmometry. Homopolymer contamination was found to be present in the lowest grafted copolymers. Poly(vinylpyridine) homopolymer was removed by its dissolution in dilute hydrochloric acid. Poly(VBP) homopolymer was removed by fractional precipitation in water/methanol mixtures. Complete removal of homopolymer is thought to be
difficult in all three cases. The molar masses and polydispersities of the graft copolymers were found to be similar to the corresponding homopolymers of poly(4-VP), poly(2-VP) and poly(VBP) produced under analogous conditions.

By applying the Jaacks simplification, and the Fineman-Ross and Kelen-Tudos methods to copolymerisation data, the reactivity ratio \( r_1 \) for the comonomer was determined for each set of copolymerisations. The values of \( r_1 \) did not appear to depend significantly on the method of estimation. Comonomer reactivities were found to be significantly higher in all copolymerisations than for conventional statistical copolymerisations. Therefore, the macromonomer reactivity is reduced compared to styrene for analogous copolymerisations.

The macromonomer reactivity was not only controlled by the end-group but also by a number of other factors. These may include possible excluded volume, incompatibility and solvent effects resulting from the influence of the macromonomer chain. It was realised that the methods used to determine \( r_1 \) only produce approximate estimates and assume the terminal model for copolymerisation is correct. Values of \( r_2 \) could not be determined with any degree of certainty as a result of the large difference between the comonomer and macromonomer mole fractions in the feed and the copolymer.

Altering the feed composition enabled a degree of control over the graft copolymer composition. Copolymerised comonomer produce the backbone of the graft copolymers, whereas copolymerised macromonomer resulted in grafts. The molar masses of the grafts was controlled by the molar masses of the macromonomer copolymerised. A number of parameters were controlled by altering the feed composition. An increase in macromonomer feed concentration produced an increase in PS content in the copolymer and therefore an increase in the number of grafts per copolymer chain. The total monomer concentration in the feed was kept approximately constant. Therefore, the comonomer concentration decreased resulting in
lower comonomer content in the copolymer and therefore lower backbone molar masses. The conversion chemical heterogeneity was small with only a small drift in composition between copolymers prepared with identical feed compositions but to different conversions.

PET particles were prepared by the step-growth reaction polymerisation of BHET using poly(VBP)-graft-PS copolymers as steric stabilisers. Particle size and morphology were estimated by SEM. Particle stability and size were found to be strongly influenced by stabiliser composition and concentration. Copolymers containing poly(4-VP) and poly(2-VP) backbones were ineffective at stabilising particles. The mechanism for stabilisation was postulated to require the formation of covalent bonds from the stabiliser backbone to the PET particle in order to prevent the desorption of the stabiliser from the particle surface at the high temperatures and shear rates observed in the polymerisation. The mechanism for polymerisation was assumed to be similar to the suspension process in aqueous media for addition polymers. These are characterised by fast stirring rates and low concentrations of stabiliser used. High molar mass PET was obtained by carrying out the polymerisation over a number of hours.

Micellar dispersions of the graft copolymers were prepared in cyclohexane, toluene and methanol. Characterisation of micelles was performed by SAXS (for poly(4-VP)-graft-PS and poly(VBP)-graft-PS) and TEM. SAXS demonstrated that the micelles in cyclohexane and toluene conform to the conventional model with a core composed of the insoluble backbone of the copolymer whilst the soluble grafts provided stabilisation by a protective layer (core-shell model). The data handling technique of Guinier has been used to determine the radius of gyration of the micellar cores and the empirical method of Koberstein et al. has been used to interpret the negative deviations from Porod's Law in terms of fringe thicknesses. The empirical method was selected over the
alternative methods on the basis of the range of applicability for estimating the fringe thicknesses for these copolymers. The variations in these two parameters have been studied for a number of the graft copolymers as a function of copolymer composition and the dispersion medium. Experiments were also performed masking the electron density of the fringe using oligostyrene to confirm the Guinier analysis determined the radius of gyration of the micelle core and not the overall Rg of core ans shell. The micelle core radius was found to be dependent on the copolymer composition. Decreasing the molar mass of the backbone produced a corresponding decrease in the radius of gyration. For poly(4-VP)-graft-PS copolymers, the radius of gyration was related to the micelle core radius, at high graft frequencies the micelle core was predicted to contain some fraction of PS grafts as well as poly(4-VP) backbones. The fringe thickness was compared to calculated chain lengths for PS in different conformations, a helix and an unperturbed chain. The better model for the PS chains in the fringe is the unperturbed model. No significant difference in micelle core radius was observed in cyclohexane compared to toluene. For poly(VBP)-graft-PS copolymers in toluene the value of Rg was related to the copolymer backbone in solution. Loose aggregates of copolymer chains in solution were predicted because of the swelling of poly(VBP) in toluene. In cyclohexane, micelle shape varied with composition, rod-like micelles being formed at moderate grafting frequencies. The highly grafted copolymer was thought to be a monomolecular micelle or in solution due to the low number of pyrrolidone units compared to styrene. For all graft copolymers with low grafting frequencies, micelles could not be produced as the area each graft was required to stabilise was too large and precipitated polymer was produced.

In methanol, highly grafted copolymers precipitated from the dispersion medium. This was considered in terms of the size of the stabilising loops and tails of backbone segments. Below
approximately $M_n$ segment = 3.0 kg mol$^{-1}$ stabilisation did not occur. The size of shape of micelles by TEM was found to be approximately independent of composition. SAXS data analysis showed a similar relationship with the determined radius of gyration being approximately constant. Porod's law behaviour showed the presence of positive deviations indicating a heterogeneous electron density profile in the core. The magnitude of these deviations decreased with increasing graft content in the copolymers. A qualitative model was proposed of the micelle structure consisting of a spherical vesicle or hollow sphere with a solvated backbone layer encasing the PS grafts outside the sphere and in the micelle core. Alternatively, the backbone and insoluble grafts were considered to contribute to the observed radius of gyration.

Free-radical dispersion polymerisations of addition monomers was successfully carried using a range of stabilisers. PMMA particles in cyclohexane were prepared using poly(2-VP)-graft-PS and poly(4-VP)-graft-PS stabilisers. Particle morphology and size were estimated using SEM and TEM respectively. Graft copolymer composition was found to strongly influence particle size and morphology. At low grafting frequencies, bridging between particles was observed under the electron microscope. This was attributed to the lower graft segment density in the stabilising layer, thus producing a weaker steric barrier. For poly(2-VP)-graft-PS stabilisers discrete particles were produced over the ASB range of 1.7:1 to 0.5:1. Copolymers with an ASB ratio of 3.6:1 did not micellise in cyclohexane. It is proposed that the limiting ASB value lies between 3.6:1 and 1.7:1. For poly(4-VP)-graft-PS copolymers produced discrete particles only at an ASB of 0.45:2. The difference in stabiliser behaviour was explained in terms of the different solubility parameters for poly(2-VP) and poly(4-VP). Micelles containing poly(4-VP) backbone will have a higher dissociation energy than poly(2-VP) and therefore the concentration of stabiliser available for surface coverage is far lower thus
leading to flocculation of PMMA particles. The concept of coalescence was proposed in determining the final particle size of the dispersion. Particle morphology showed that the PMMA particles were composed of a large number of smaller particles. Coalescence occurred due to insufficient free stabiliser being present to cover bald patches as they appear on the growing primary particles. A number of parameters were found to influence particle size and distribution. No significant variation of particle size was found by using seed/feed versus one shot methods. Increasing monomer concentration increased the final particle size and also widened the size distribution. An increase in stabiliser concentration produced smaller particles. The lower limit for the formation of discrete particles was found to be approximately 1% by weight stabiliser. Increasing the initiator concentration was found to increase the size of the particles. This was explained using conventional nucleation theories in conjunction with the concept of coalescence. The surface coverage of discrete PMMA particles was calculated and was represented as the surface area A occupied or stabilised by each PS graft. The mean separation distance d between adjacent PS chains was calculated assuming hexagonal close packing at the particle-liquid interface. A and d were found to vary according to the copolymer composition. Highly grafted copolymers had a smaller distance between adjacent grafts. The conformation of the backbone segments was estimated with the knowledge of graft spacing and the molar mass of the backbone segments. Poly(4-VP) was found to be compatible with PMMA indicating that the backbone is incorporated into the particle and does not lie just on the surface. Dispersions flocculated upon the addition of methanol a non-solvent for the PS chains, suggesting that the mechanism was steric stabilisation provided by a surface layer of PS. No stable dispersions of PMMA were obtained using poly(VBP)-graft-PS as stabilisers.
Stable dispersions of poly(4-VP) in toluene and cyclohexane and poly(2-VP) in cyclohexane were obtained. Graft copolymer composition was found to significantly influence the effectiveness of the stability and size of the particles produced. Poly(4-VP)-graft-PS copolymers did not produce stable dispersions of poly(4-VP) in cyclohexane. This was explained in terms of the higher dissociation energy required for the micelles and the smaller size of the primary particles formed, thus leading to bald spots appearing on the growing particles which were not covered by free stabiliser and which subsequently coalesced and flocculated. Particle size in toluene was found to be close to the minimum particle size obtainable at 5% dispersant level indicating that the efficiency of the anchoring mechanism was high and little or no coalescence of particles had occurred. Stabiliser concentration was found to influence particle size in a similar manner to PMMA/Cyclohexane. Higher concentrations produced smaller particles. Poly(4-VP) particles stabilised by poly(2-VP)-graft-PS were found to be stable in cyclohexane and toluene. The particles were larger than comparable particles stabilised with poly(4-VP)-graft-PS. This was explained by the solubility of the graft copolymer in toluene instead of its micellisation. SAXS on a poly(4-VP) particles stabilised with poly(4-VP)-graft-PS were carried out. The radius of gyration and thus the core radius \( D_c \) of the particles was determined using the method by Guinier. The fringe thicknesses were also calculated using the empirical approximation for negative deviations from Porod's law. The particle core radius was found to be larger than the value determined by TEM. The fringe thickness was found to be similar to the chain dimensions for an unperturbed PS chain. But at high graft frequencies chain extension was observed indicating that some elongation of the PS grafts occurs due to the net repulsive effects of neighbouring PS segments. All these dispersions were found to be stable over long periods of time. Flocculation occurred rapidly by the
addition of a non-solvent, indicating that the mechanism is steric stabilisation.

Stable dispersions of PS in methanol were obtained using all types of graft copolymer stabiliser. Highly grafted copolymers were not effective as the stabilising loops and tails were not long enough to provide a large steric barrier. Poly(VBP)-graft-PS at the lowest graft frequency was effective. Higher amounts of grafting lead to precipitated PS, this was thought to be due to the soluble copolymer backbone containing styrene units which probably interact with the styrene groups present in the particle thus providing only a weak steric barrier. Poly(4-VP)-graft-PS and Poly(2-VP)-graft-PS copolymers were both effective stabilisers. Copolymer composition was found not to significantly influence particle size, although it was noted that there is a difference in size between the two series of copolymers. A similar trend was observed when homopolymers of poly(2-VP) and poly(4-VP) were used as stabilisers. This was attributed to the difference in solubility parameter between poly(4-VP) and poly(2-VP). Methanol is a better solvent for poly(4-VP) having greater chain extension and thus being able to stabilise a larger area of the particle. The mechanism for stabilisation for the homopolymers was thought to be different to the graft copolymers. Radical grafting of growing PS chains is thought to occur leading to the in-situ formation of graft copolymers which can subsequently be used to stabilise growing particles. Particle size was found to be influenced by the use of seed/feed methods compared to one shot methods and the level of stabiliser concentration. Graft copolymer stabilised particles are predicted to have undergone little or no coalescence since the particle size is close to the minimum size obtainable with a 5% by weight dispersant level, indicating a highly efficient anchoring mechanism. This is likely as the core particle and anchoring grafts are of the same chemical composition. Homopolymer stabiliser concentration affected the particle size in a similar manner, with small
particles being produced at higher concentrations. The molar mass of the stabiliser was found not influence the particle size. All particles exhibited long term dispersion stability, and with the addition of a non-solvent flocculation occurred, indicating steric stabilisation was the predominant mechanism.
7. RECOMMENDATIONS FOR FURTHER WORK

The present work has provided a method for preparing well-defined graft copolymers suitable for the steric stabilisation of PMMA and poly(VP) dispersions. Stabilising PS chains with molar masses of $M_n = 3.0$ kg.mol$^{-1}$ provided layers of sufficient thickness to prevent flocculation. Backbone molar masses of 10-30 kg.mol$^{-1}$ were sufficient to provide anchoring to the particle. However, further work is required to determine more fully the conformation of the anchoring component and the stabilising PS chains. Small-angle neutron scattering of micelles and particles is a useful technique to determine the conformation of the anchor component and the stabilising chains. Only a few experiments were performed to determine the depth of the steric layer using SAXS, more experiments need to be carried out to perform an indepth study of the influence of different grafting frequencies on the conformation of the PS chains on different particles. Rheological studies could be performed in order to determine the surface layer thickness which could be compared to the fringe thickness determined by SAXS although the errors involved may be considerable due to the small layer thicknesses involved. Controlled flocculation studies on dispersions need to be performed by adding a non-solvent for the stabilising chains, in order to determine the critical flocculation temperature and critical flocculation volume. This could then be related to the $\Theta$-conditions for the stabilising chains in order to confirm a steric stabilisation mechanism is operative. PS chains in cyclohexane have a theta temperature of 308K. Flocculation of PS stabilised dispersions is predicted to occur close to this point, although as noted earlier they were stable at room temperature. Dispersions of PS particles in methanol have been successfully made using both homopolymers and graft copolymers. Further work is required to determine the probability of radical grafting of growing PS chains onto the homopolymer to form in-situ graft copolymers which then are adsorbed by the precipitating nuclei to form
sterically stabilised particles. Preliminary work on the solution polymerisation of styrene in the presence of poly(4-VP) was performed but it was found difficult to purify the resulting mixture of PS and poly(4-VP). A more in depth investigation is required to study particle formation and the size and number of these primary particles. This evidence would aid further understanding into the mechanism by which coalescence occurs. The influence of solvency on the dispersion medium needs to be investigated to study its effect on the size and number of nuclei formed.

For the graft copolymers prepared from the copolymerisation of comonomer ($M_1$) with PS macromonomer ($M_2$), only $r_1$ was determined as a result of the high degree of uncertainty in determining $r_2$. It would be informative to determine $r_2$ in order to estimate the macromonomer reactivity and whether the assumptions made in section 5.4.3 were correct. Values of $r_2$ could be determined if the molar feed concentration was high enough. Ideally the copolymer compositions would be measured indirectly by measuring macromonomer and comonomer conversions accurately. It would be informative to carry out copolymerisations in mixed solvents, i.e. DMF/toluene to study the change (if any) in reactivity ratios. This would assist in determining whether solvent effects altered macromonomer reactivity. Comparison of the copolymerisation of macromonomers with higher and lower molar masses would be useful in studying the influence of the macromonomer chain on reactivity (the excluded volume effect). No problems would be encountered synthesising macromonomers with a lower molar mass, and characterisation would indeed be easier. The converse is true for high molar mass macromonomers, end group detection becomes increasingly difficult and subject to larger errors.

Purification of graft copolymers with higher molar mass grafts would be more complicated due to the difficulty in separating unreacted macromonomer from graft copolymer. The copolymerisation of styrene with poly(2-VP) macromonomers has
been documented, although no detailed copolymerisation data analysis was performed. The copolymerisation of styryl-terminated poly(VP) macromonomer with styrene would highlight the difference in reactivity ratio for the macromonomer compared to the comonomer which if the terminal model is correct should be 1 for both species.

The use of macromonomers directly in dispersion polymerisations of addition polymers as stabiliser precursors has been widely documented\textsuperscript{228} with the formation of the graft copolymer in situ. The anchor components would have the same chemical composition as the dispersed phase. Such methods have not been used in the dispersion polymerisation of PET. The use of a diol terminated polyethylene macromonomer would be effective for the formation of in-situ graft copolymer stabilisers. Alternatively poly(12-hydroxystearic acid) could be used as the macromonomer chain.

The study of micelle formation in a number of different dispersion medium has been performed. SAXS has proved to be a useful technique in determining micelle structure. A number of questions remain unanswered about the interpretation of the SAXS data. Micellar dispersions in cyclohexane and toluene have been shown to possess the conventional core-shell structure, similar to the behaviour of block copolymers. Further work is required to determine the conformation of the copolymer backbone chains in the micelle core and the stabilising PS chains in the fringe. This may lead to a more detailed understanding of the possible contribution to the core of unsolvated PS grafts. It would be interesting to study the change in micelle structure by increasing the number of grafts in the copolymer even further. High graft frequencies will lead to smaller micelle core radius and the possibility of higher amounts of unsolvated PS contributing to the core structure. Increasing the molar mass of the PS stabilising chains but keeping the mole ratio of grafts to backbone the same is predicted to increase the fringe thickness. At high enough
molar mass of grafts a three phase system may occur with a micelle core composed of copolymer backbone and a large solvated shell of PS stabilising chains. This model was proposed by Plestil and Baldrain\textsuperscript{202} for a block copolymer with 75\% by wt. polybutadiene stabilising block, they interpreted the data as a double Guinier plot. It would be interesting to see if this interpretation was correct or the Porod' law behaviour holds. Alternatively, the micelle core may contain unsolvated grafts and have a layered structure with a lower than predicted fringe thickness. The study of micelle formation of polystyrene-graft-poly(VP) copolymers in cyclohexane and toluene would be an interesting comparison, with the grafts forming the insoluble segment as in the micellar experiments performed in methanol. These experiments may provide further evidence of a hollow sphere model or the validity of the backbone contributing to the micelle core. Further work is required to confirm the plausibility of the models for poly(VP)-graft-PS copolymers in methanol. \textsuperscript{1}H nmr and small-angle neutron scattering experiments could provide structural information on the micelle. It was proposed in section 5.5.2. that a multiblock copolymer may form similar hollow sphere structures. The graft copolymers in their bulk state have only been analysed by DMTA, which led to a proposed model of domains of one region in a matrix of the other, SAXS and TEM could be used to determine the size of these domains and their relationship with micelle formation.

The graft copolymer structures proposed above could all be assessed for the effectiveness as steric stabilisers in dispersion polymerisation of addition polymers in a variety of different dispersion media. By reversing the graft and backbone chemical composition, the major mode of stabilisation of PMMA particles in cyclohexane is proposed to be by loops and tails of PS. It would be interesting to observe the final particle size and whether coalescence is predicted. The lower limit for the ASB value could be determined for PMMA in cyclohexane and
poly(VP) in toluene by increasing the graft content in the copolymer.

The above recommendations may lead to a more quantitative theoretical understanding of micelle formation and the mechanism of steric stabilisation.
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