Characterisation of molecular weight and compositional heterogeneity in block copolymers

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CHARACTERISATION OF MOLECULAR WEIGHT AND COMPOSITIONAL HETEROGENEITY IN BLOCK COPOLYMERS

by

THOMAS DUMELOW

A Doctoral Thesis

Submitted in partial fulfilment

of the requirements for the award of

Doctor of Philosophy

of the Loughborough University of Technology

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ABSTRACT

A gel permeation chromatography (GPC) system, using two concentration detectors and a low angle laser light scattering (LALLS) detector, has been investigated for use in characterising copolymers. At each elution volume, the system allows the calculation of molecular weight, average composition, and compositional heterogeneity. Overall molecular weight, composition, and heterogeneity parameters can also be calculated. This characterisation method yields heterogeneity information previously unobtainable without the use of cross fractionation techniques which are far more time consuming but ultimately more thorough.

The system has been tested using polystyrene/polydimethylsiloxane (PS/PDMS) blends and diblock copolymers in tetrachloroethylene (TTCE). The blend results were in good agreement with theory and compared favourably with static LALLS results obtained in this study. However, concentration detector inconsistencies dictated that the GPC results were inaccurate at the low molecular weight end of the chromatograms. The technique was used to show that some of the "copolymer" samples investigated contained a high proportion of homopolymers. The calculated compositional heterogeneity of other samples accurately agreed with the random coupling statistics expected from block copolymerisation.

For the most accurate results, samples should have high molecular weights and their component refractive indices should be significantly different, the solvent refractive index preferably falling between the two component values. It is also desirable that the two component molecular weight column calibrations should be similar over the molecular weight range of the samples considered.
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CHAPTER 1

INTRODUCTION
Molecular weight is a fundamental property of all polymers. It directly affects physical properties in many ways which are vital to a polymer's application or processing\(^1,2\). It will, for example, influence the melt flow characteristics, solution properties, crystallinity, and mechanical properties.

The correlation between molecular weight and physical properties makes the measurement of molecular weight very important. This measurement can also be used as a tool in investigating polymerisation reactions. A single number, however, can never fully describe the molecular weight, or the molecular weight related properties, of a sample. This is because a typical polymer contains a range of molecular weights. The only way to fully describe a polymer molecular weight is in terms of a molecular weight distribution\(^3\).

In the case of copolymers the situation is further complicated by the fact that both molecular weight and composition distributions will be present. A full knowledge of both these distributions and how (or if) they are correlated can be used in investigating copolymerisation kinetics (or may simply be used to show how successful a particular copolymerisation reaction has been). Physical properties will also be affected by all the above factors. There is a good deal of information to be gained, therefore, given the right technique.

A limited amount of information on the two distributions can now be obtained fairly routinely, but techniques for completely characterising both distributions simultaneously have inevitably been very time consuming\(^4\). This study attempts to develop a relatively fast technique, using standard equipment, which fully describes the molecular weight distribution and simultaneously gives a large amount of information about the composition distribution.
Section 1.1

Molecular Weight Characterisation of Polymers

Since any polymer sample will contain molecules covering a range of molecular weights, most techniques either measure only an average molecular weight or make use of a separation mechanism to obtain a molecular weight distribution.

Non-separation techniques, in the main, provide a value for a particular form of average molecular weight. Light scattering is the technique generally most applicable to higher molecular weight polymers. It provides an absolute measure of the weight average molecular weight, $M_w$, of the polymer, defined as

$$M_w = \frac{\sum N_i M_i^2}{\sum N_i M_i}$$ (1.1.1)

where $N_i$ is the number of molecules of molecular weight $M_i$ in the sample.

Most other absolute techniques measure the number average molecular weight, $M_n$, defined as

$$M_n = \frac{\sum N_i M_i}{\sum N_i}$$ (1.1.2)

Such techniques depend either on measuring colligative properties in dilute solution, e.g. freezing-point depression, vapour-pressure lowering, boiling point elevation, and osmotic pressure, or on end-group analysis. Of all these techniques only membrane osmometry is appropriate to higher molecular weight polymers (>20,000). It is, however, a slow technique unless sophisticated equipment is used, and if an absolute $M_n$ value is not needed, other molecular weight techniques are easier.

A relatively quick and easy technique is viscometry. It is not absolute, but it may be calibrated to provide average molecular weight values applicable to a given solvent-temperature system.
The technique most appropriate to molecular weight separation is, for almost all polymers, gel permeation chromatography (GPC). This separates molecules according to their size in solution. It is a secondary technique in that it requires a calibration of the system using polymer standards of known molecular weight.

The two molecular weight characterisation techniques of interest in this study are light scattering and GPC.

1.1.1. Light Scattering

A typical classical light scattering instrument requires a light source to be focused into a sample cell containing a solution of the polymer to be investigated. Scattered light is detected by a photomultiplier which can be moved around the cell to detect the light intensity over a series of scattering angles. It is necessary to obtain readings over a number of concentrations and angles for each molecular weight determination. The results must then be extrapolated to zero angle and concentration.

Because extrapolation to zero angle is necessary it is important that light scattering instruments should be capable of giving low angle readings. Traditionally the range of commercially available light scattering instruments would not extend below 30°, although in 1961 Katz reported measurements down to 90° with his own instrument. Considerable effort has been put into obtaining low angle instruments, such as those constructed by Meyerhoff et al. or by Utiyama and Tsunashimi. The main problems encountered were due to geometrical restrictions and the high background scatter (e.g. from dust particles) present at low angles. The technique of low angle laser light scattering (LALLS) largely overcame both of these problems. The basic optical system of a LALLS photometer is shown in Figure 1.1.1. This has a much smaller scattering volume than classical instruments so that any foreign particle which enters it is easily identified as such. The low angle scatter is measured by
focusing through an aperture the scattered light that has passed through the annulus. Although it is possible to alter the scattering angle by selecting different annuli, in practice this is not necessary as the angles are sufficiently low for angular dependence to be ignored. Scatter can actually be measured down to 2°, but a wider annulus is usually used to minimise background scatter. Thus it is only necessary to take readings at one angle and a few concentrations to obtain an $M_w$ value, and typically a complete determination takes only one or two hours.

1.1.2. Gel Permeation Chromatography

The term gel permeation chromatography was first used by Moore, who applied gel separation techniques to polymer solutions in organic solvents. He used a semi-rigid crosslinked polystyrene gel packed into chromatographic columns to give comparatively rapid and reliable separations. The chromatograph assembly described by Maley gives an indication of the basic instrumental requirements. A typical modern GPC instrument would contain

(a) a pumping system supplying a controlled flow of solvent;

(b) an injection system which injects a small quantity of sample solution into the solvent flow;

(c) the GPC columns which separate the sample molecules according to their size in solution, the largest molecules being eluted through first;

(d) a concentration detector.

Modern GPC packings allow the use of short columns, so that a complete run can normally be completed without difficulty in under an hour.
It is usual to calibrate the GPC columns in terms of molecular weight, using narrow molecular weight distribution standards. Thus each time interval from injection, or elution volume, will be assigned a particular molecular weight value. However, since GPC separates according to molecular size rather than molecular weight, such a calibration is strictly speaking only applicable to that particular polymer type. Conversions to the equivalent molecular weight of other polymer types are often performed, however, when the appropriate parameters are known for these particular types. Reliable values of these parameters may not be available. When they are not, GPC is still extremely useful for simply comparing molecular size distributions of more than one polymer of the same type.

A direct method of absolute molecular weight determinations from GPC is to use a chromatograph having a LALLS photometer connected on line, as shown in Figure 1.1.2. A continuous measure of the molecular weight of the molecules emerging from the columns is then possible.
The basic optical system of a LALLS photometer.
Figure 1.1.2. A typical GPC/LALLS chromatographic system.
Section 1.2

Copolymer Characterisation

Copolymer samples will have, in general, not only a molecular weight distribution, but also a simultaneous distribution of compositions. Many copolymers will also exhibit further distributions, such as in sequence length. Thus a full characterisation must be complex, and a graphical representation would require at least three dimensions.

1.2.1. Light Scattering

Only in the exceptional cases, when all molecules are identical in composition, or both components have the same refractive index, will light scattering give a true $M_w$ value from measurements in a single solvent. The deviation from the true $M_w$ value will depend on the copolymer compositional heterogeneity and the difference between solvent and copolymer refractive indices. Theory predicts that, by using three solvents of differing refractive index, sufficient information should be gained to yield a true $M_w$ value and an indication of the extent of compositional heterogeneity. Such an analysis has been successfully used on all types of copolymers, the theory fitting best to block copolymers.

1.2.2. Gel Permeation Chromatography

Two problems arise in attempting to use GPC in the molecular weight characterisation of copolymers. Firstly, the response of most concentration detectors is composition dependent, so that a distorted plot will be obtained for any copolymer sample whose average composition varies with molecular weight. Secondly, any column calibration will be unique to copolymers of the type and composition being measured.
The first problem can, in practice, be turned to advantage. \textsuperscript{27} Terry and Rodriguez \textsuperscript{27} were able to make two separate runs on a copolymer using an infrared (IR) detector. Each run was set on a frequency whereby only one component of the copolymer would be detected. The detector would have to be calibrated at each frequency using homopolymer solutions. At each elution volume, therefore, not only can the copolymer concentration be calculated, but also the concentration of each component and the average composition.

Runyon et al.\textsuperscript{28} used refractive index (RI) and ultraviolet (UV) detectors in series for the GPC analysis of styrene/butadiene copolymers. The RI detector measures both components, whereas the UV detector is sensitive only to the concentration of styrene units. The use of a spectroscopic detector in combination with an RI detector has since become fairly common practice when performing GPC analyses on copolymers.\textsuperscript{29-33}

At each elution volume there is likely to be a range of compositions and, to a lesser extent, a range of molecular weights. There are three possible approaches to assigning molecular weight values (or, more correctly, average molecular weight values) to each elution volume:

(a) express all molecular weights as "equivalent" to a homopolymer (usually polystyrene) column calibration;

(b) derive a calibration mathematically from both the component homopolymer calibrations (obtained directly or mathematically derived from a single calibration);

(c) using an on-line molecular weight detector.

The first approach is often sufficient for comparative purposes, but may produce distorted distributions and will not give correct molecular weights.
The second approach requires the use of certain theoretical
assumptions. However, it usually gives satisfactory results for
block copolymers.\textsuperscript{34}

For the third approach, a LALLS photometer may be used
as an on-line molecular weight detector, but, due to the possibility
of compositional heterogeneity may give erroneous results. Another
possibility is to use an automatic viscometer\textsuperscript{35}. Suitable instru-
ments are not commercially available at present, however.

A GPC system using two concentration detectors can thus be
made to yield the following information:

(a) average composition at each elution volume;
(b) concentration at each elution volume;
(c) average molecular weight at each elution volume.

Only recently has there been any attempt to look at the com-
positional heterogeneity at each elution volume. One approach is to
use a form of compositional separation chromatography on samples
of effluent eluting at various times. Thus a series of fractions can
be collected and each one separated out according to composition
using, for instance, thin layer chromatography (TLC)\textsuperscript{36}. An alter-
native is to fractionate according to composition first, then apply
GPC to the fractions\textsuperscript{4}. In either case, a complete characterisation
is extremely time consuming, and a preparative scale experiment is
needed.
CHAPTER 2

THEORY
Section 1.3

Aims of Present Work

This work investigates the feasibility of a GPC system, using standard equipment, which will characterise copolymers in terms of molecular weight distribution, composition, and compositional heterogeneity. A GPC instrument having two on-line concentration detectors and a LALLS detector is used.

At each elution volume the copolymer concentration and average composition are calculated from the concentration detector responses, and the average molecular weight from the individual component homopolymer column calibrations. The LALLS detector will also yield a molecular weight value, but this will, in general, be different from the true value, due to compositional heterogeneity. Assuming that there is not a large variation in molecular weight at each elution volume, a measure of compositional heterogeneity can be obtained by comparing the LALLS apparent molecular weight value with that obtained from column calibrations. This method should achieve a GPC copolymer characterisation which includes information on compositional heterogeneity unobtainable from straightforward dual detector GPC. It does not, however, have the time consuming or large scale nature of techniques requiring re-fractionation of collected chromatographic fractions.

Samples of polystyrene/polydimethylsiloxane (PS/PDMS) block copolymers which had previously been partially characterised were available when this work was started, so the study has concentrated on these copolymers and PS/PDMS blends.
Section 2.1

Light Scattering from Solutions 1: Introduction

The scattering of light by a substance involves inducing oscillating dipoles in its molecules. Energy can be re-radiated away from the incident beam if the medium is not uniformly polarisable. Thus any fluid will, because of inhomogeneities in dielectric constant, cause some scattering of light. If the scattered radiation is at the same frequency as the incident radiation the scatter is elastic.

For a single scattering centre, using non-polarised light, the scattered light intensity I is given by:

\[ I = I_0 \frac{8\pi \alpha A^2}{\lambda^2 r^4} (1 + \cos^2 \theta) \]  

(2.1.1)

where

- \( I_0 \) = incident light intensity at distance \( r \) from the scattering centre
- \( \alpha \) = polarisability
- \( \lambda \) = wavelength of light
- \( \theta \) = scattering angle measured from the incident beam

2.1.1. Fluctuation Theory

Debye\(^{37}\) considered a solution as made up of many small elements of volume. Any chosen volume element \( \delta V \) can be thought of as a scattering element of fluctuating dielectric constant (due to concentration fluctuations), surrounded by a homogeneous medium of dielectric constant \( <\varepsilon> \), i.e. the mean value. Scatter will be produced by the excess dielectric constant of the volume element, \( \Delta \varepsilon = \varepsilon - <\varepsilon> \), when \( \varepsilon \) is the instantaneous value. In equation 2.1.1, the polarisability \( \alpha \) must be replaced by the excess polarisability.

\[ \Delta \alpha = \frac{\delta V}{4\pi} \Delta \varepsilon \]  

(2.1.2)
Therefore we get on average

\[
\frac{I}{I_0} = \frac{\pi^2 \delta V^2}{2 \lambda^4 r^2} < \Delta \epsilon^2 > (1 + \cos^2 \theta) \tag{2.1.3}
\]

A more useful quantity, which is independent of distance from scattering centre, is the Rayleigh factor \( R_\theta \), defined over a scattering volume \( V \) as

\[
R_\theta = \frac{\pi^2 I}{VI_o} \tag{2.1.4}
\]

Therefore, in the case of the small scattering volume \( \delta V \) considered above

\[
R_\theta = \frac{\pi^2 \delta V}{2 \lambda^4} < \Delta \epsilon^2 > (1 + \cos^2 \theta) \tag{2.1.5}
\]

We now consider scattering due to solute alone. \(< \Delta \epsilon^2 >\), representing fluctuation due to changes in solute concentration, can be expressed as

\[
< \Delta \epsilon^2 > = \left( \frac{d\epsilon}{dc} \right)^2 < \Delta c^2 >
\]

\[
= \left( \frac{\partial \epsilon}{\partial c} \right)_T^2 \frac{kT}{(d^2 F/ dc^2)} \tag{2.1.6}
\]

where

\( c = \) solute concentration

\( T = \) absolute temperature

\( F = \) Helmholtz free energy

\( k = \) Boltzmann's constant

It may also be shown that

\[
\left( \frac{\partial^2 F}{\partial c^2} \right)_T = \frac{\delta V}{c} \left( \frac{\partial \Pi}{\partial c} \right)_T \tag{2.1.7}
\]
where \(\Pi\) represents the osmotic pressure. Thus the excess Rayleigh factor \(\overline{R}_\theta\) resulting from fluctuations in solute concentration is given by

\[
\overline{R}_\theta = \frac{\pi^2 (\partial \varepsilon / \partial c)^2}{2 \lambda^4 (\partial \Pi / \partial c)} T^2 \ k T c \ (1 + \cos^2 \theta) \tag{2.1.8}
\]

Thus it can be seen that \(\overline{R}_\theta\) does not depend on \(\delta V\) and applies throughout the solution.

The dielectric constant may be related to the square of the refractive index \(n\). Therefore

\[
\left( \frac{\partial \varepsilon}{\partial c} \right)^2_T = 4n^2 \left( \frac{\partial n}{\partial c} \right)^2_T \approx 4n_o^2 \left( \frac{\partial n}{\partial c} \right)^2_T \tag{2.1.9}
\]

where \(n_o\) is the solvent refractive index, \(\left( \partial n / \partial c \right)_T\) being known as the refractive index increment of the solution. We can now write the excess Rayleigh factor as

\[
\overline{R}_\theta = \frac{KRTc}{\left( \partial \Pi / \partial c \right)_T} \tag{2.1.10}
\]

where

\[
K = \frac{2\pi n_o^2 (\partial n / \partial c)_T^2}{\lambda^4 N} (1 + \cos^2 \theta)
\]

\(N = \) Avogadro's number
\(R = \) gas constant

For an ideal solution of molecules of molecular weight \(M\),

\[
\Pi = \frac{RTc}{M} \tag{2.1.11}
\]

\[
\therefore \overline{R}_\theta = KcM \tag{2.1.12}
\]

This equation could thus be used to give a direct measurement of molecular weight, assuming \(\left( \partial n / \partial c \right)_T\) is known. However, Doty et al.\(^38\) have pointed to the osmotic pressure observations of Flory\(^39\) to show that ideality cannot be assumed for high molecular
weight polymer solutions even at very low concentrations. Thus the osmotic pressure must be expressed as an expansion of the form

\[ \Pi = RT\left(\frac{c}{M} + A_2c^2 + A_3c^3 + \ldots \right) \]  \hspace{1cm} (2.1.13)

where \( A_2, A_3, \ldots \) are osmotic virial coefficients, causing the solution to deviate from ideality as investigated by McMillan and Mayer. We therefore get

\[ \left( \frac{\partial \Pi}{\partial c} \right)_T = RT\left( \frac{1}{M} + 2A_2c + 3A_3c^2 + \ldots \right) \] \hspace{1cm} (2.1.14)

Equation 2.1.12 now becomes

\[ \frac{K_c}{R_\theta} = \frac{1}{M} + 2A_2c + 3A_3c^2 + \ldots \] \hspace{1cm} (2.1.15)

In practice only the first two terms are considered, as higher terms get vanishingly small. Extrapolation to zero concentration gives equation 2.1.12.

The above theory applies to monodisperse polymer solutions. Zimm and Doty showed in 1944 that for a polydisperse polymer solution, assuming additivity of \( R_\theta \) values for all the molecules, such an extrapolation will give the weight average value of the molecular weight.

Despite Zimm and Doty's observations, it was not until 1949 that any rigorous theory for polydisperse systems was developed, when it was shown that equation 2.1.15 is essentially unchanged. However \( M \) must be replaced by \( M_w \) and \( A_2 \) is no longer the same as the osmotic second virial coefficient. The standard light scattering formula is therefore

\[ \frac{K_c}{R_\theta} = \frac{1}{M_w} + 2A_2c \] \hspace{1cm} (2.1.16)
2.1.2. Distribution Function Theory

Fluctuation theory considers each molecule as a single scattering centre. For large molecules, however, intramolecular interference is likely to reduce the amount of scatter. The theory developed by Zimm, Albrecht, and Yamakawa considers each molecule as made up of a number of scattering units, and is able to take such interference into account.

Thus for a molecule of N scattering units, a factor \( P(\theta) \) can be calculated to represent the reduction in the scattered intensity at scattering angle \( \theta \) due to destructive interference, averaged over all orientations:

\[
P(\theta) = \frac{1}{N^2} \sum_{i} \sum_{j} \frac{\sin kr_{ij}}{kr_{ij}}
\]

(2.1.17)

where \( k = \frac{4\pi}{\lambda} \sin \left( \frac{\theta}{2} \right) \)

\( \lambda' \) = wavelength of light in the scattering medium.

For a deformable particle such as a polymer molecule a time average of \( P(\theta) \) is needed. Although the distribution function approach uses only electromagnetic theory, the overall effect on a solution of identical molecules is to use \( P(\theta) \) as a correction to \( R_g \) in the infinite dilution limit of equation 2.1.15:

\[
\lim_{c \to 0} \left( \frac{KC}{R_g} \right) = \frac{1}{P(\theta)M}
\]

(2.1.18)

\( P(\theta) \) can be expanded as a power series:

\[
P(\theta) = \frac{1}{N^2} \left( N^2 - \frac{1}{3!} \sum_{i} \sum_{j} k^2 r_{ij}^2 + \frac{1}{5!} \sum_{i} \sum_{j} k^4 r_{ij}^4 \ldots \right)
\]

(2.1.19)

The mean-square radius of gyration \( \langle s^2 \rangle \) of a polymer chain may be related to \( r_{ij} \) by:

\[
\langle s^2 \rangle = \frac{1}{2N^2} \sum_{i} \sum_{j} r_{ij}^2
\]

(2.1.20)
Therefore:

\[ P(\theta) = 1 - \frac{1}{3} k^2 <s^2> + \ldots \]

\[ = 1 - \frac{1}{3} \left(\frac{4\pi}{\lambda} \right)^2 <s^2> \sin^2 \left(\frac{\theta}{2}\right) + \ldots \]  

Equation 2.1.18 then becomes:

\[ \lim_{c \to 0} \left( \frac{Kc}{R_\theta} \right) = \frac{1}{M} \left[ 1 + \frac{16\pi^2}{3(\lambda')^2} <s^2> \sin^2 \left(\frac{\theta}{2}\right) + \ldots \right] \]  

Therefore light scattering is useful not only in determining molecular weight, but also the mean-square radius of gyration.

The theory is not restricted to identical molecules or the zero concentration limit. Equation 2.1.18 can be replaced by:

\[ \frac{Kc}{R_\theta} = \frac{1}{P(\theta)M_w} + 2A_c c + \ldots \]  

where \( P(\theta) \) has the same form as \( P(\theta) \) shown in equation 2.1.21, but \( <s^2> \) is replaced by \( <s^2>_z \), the z-average value of the mean-square radius of gyration, defined as:

\[ <s^2>_z = \frac{\sum M_i <s^2>_i \gamma_i}{\sum M_i \gamma_i} \]  

where \( <s^2>_i \) is the mean-square radius of gyration of the homogeneous polymer of molecular weight \( M_i \), and \( \gamma_i \) is its weight fraction.

At the low angle limit equation 2.1.23 reduces to the form derived from fluctuation theory, i.e. equation 2.1.16.

2.1.3. **Molecular Weight Determination**

The traditional approach to molecular weight determination using light scattering has been to take a large number of readings at
varying angles and concentrations. The results of these measurements would be plotted on a Zimm plot\textsuperscript{47}, an example of which is illustrated in Figure 2.1.1. A plot is made of $Kc/\overline{R}_g$ against $\sin^2(\theta/2) + nc$, where the value of $n$ has no significance and is chosen for convenience. From equation 2.1.23 one can see that extrapolation to zero angle and concentration will give an intercept $1/M_w$, and the initial slope of the $c = 0$ curve can be used to measure the mean-square radius of gyration.

At the low angles obtainable using a LALLS photometer, however, angular variation can be ignored, and equation 2.1.23 reduces to equation 2.1.16. By taking readings at a few concentrations, therefore, and plotting $Kc/\overline{R}_g$ against $c$, one obtains a graph of slope $2A_2$ and intercept $1/M_w$. 
Figure 2.1.1. A typical Zimm plot. See text for meaning of symbols.
Section 2.2.

Light Scattering from Solutions 2: Copolymers

As long ago as 1950, deviations in measured molecular weights were noted using light scattering measurements on copolymer solutions having low \( \left( \frac{2\kappa}{\kappa_c} \right)_T \) values. It was suggested that this may be due to compositional inhomogeneity in the copolymer, and that light scattering measurements in a series of solvents may in fact serve as a measure of such inhomogeneities. The basic theoretical work was started by Stockmayer et al. and developed by Benoit with various associates as reviewed in 1972.

2.2.1. Basic Theory and Introduction

It is convenient to start with Debye's original light scattering expression (equation 2.1.12) written in a slightly different form:

\[
\bar{R}_g = K^* c M \nu^2
\]

(2.2.1)

where \( K^* = \frac{2\pi n_0^2}{N} \frac{1}{\lambda^4} \)

\( \nu = (\partial n/\partial c)_T \)

all symbols being those defined in Section 2.1.

Thus, low angles and infinitely low dilution have been assumed.

For a polydisperse homopolymer equation 2.2.1 becomes

\[
\bar{R}_g = K^* \nu^2 \sum_i c_i M_i
\]

\[
= K^* c M_w \nu^2
\]

(2.2.2)

In the case of copolymers each molecule will have its own \( \nu_i \), which depends on its composition. Therefore
\[
\bar{R}_\theta = K^* \sum_{i} c_i M_i \nu_i^2
\]

(2.2.3)

\[
\bar{M}_w \text{ in equation 2.2.2 must be replaced by an apparent average molecular weight } M^*:
\]

\[
\bar{R}_\theta = K^* c M^* \nu^2
\]

(2.2.4)

where \(\nu\) is the refractive index increment of the solution. The apparent average molecular weight \(M^*\) is given by

\[
M^* = \frac{1}{c \nu^2} \sum_{i} c_i M_i \nu_i^2
\]

\[
= \frac{1}{\nu^2} \sum_{i} y_i M_i \nu_i^2
\]

(2.2.5)

where \(y_i\) is the weight fraction of molecules of type \(i\):

\[
y_i = \frac{c_i}{\sum_i c_i}
\]

(2.2.6)

\(M^*\) can be seen to vary with \(\nu\), i.e. it varies from solvent to solvent. We must now examine how \(M^*\) varies with composition.

Consider a monodisperse copolymer containing only two types of unit, A and B. Then, the composition by weight is defined as

\[
W = \frac{M_A}{M_A + M_B}
\]

\[
= \frac{C_A}{C_A + C_B}
\]

(2.2.7)

where \(M_A\) and \(M_B\) represent the molecular weights of the polymers formed by the A and B groups respectively, and \(C_A\) and \(C_B\) are their respective concentrations. For a polydisperse copolymer

\[
W = \frac{C_A}{C_A + C_B}
\]
One now assumes a linear variation of refractive index increment with composition, i.e.
\[ \nu = W \nu_A + (1 - W) \nu_B \]  
(2.2.9)
where \( \nu_A \) and \( \nu_B \) are the refractive index increment of the A and B units respectively.

Similarly, when considering molecules of type \( i \),
\[ \nu_i = W_i \nu_A + (1 - W_i) \nu_B \]  
(2.2.10)
where \( W_i \) is the composition of molecules of type \( i \). Thus \( M^* \) becomes
\[ M^* = \frac{1}{2} \sum_i W_i \nu_A M_i + (1 - W_i) \nu_B M_i + \sum_i 2 W_i (1 - W_i) \nu_A \nu_B M_i \]  
(2.2.11)

By introducing the term \( \delta W_i = W_i - W \), the deviation in composition of molecules of type \( i \) from the overall composition, equation 2.2.11 can be rewritten as
\[ M^* = \bar{M}_w + 2P \left( \frac{\nu_A - \nu_B}{\nu} \right) + Q \left( \frac{\nu_A - \nu_B}{\nu} \right)^2 \]  
(2.2.12)
where
\[ P = \sum_i W_i \delta W_i \]
\[ = \frac{1}{2} \left[ (1 - W) (\bar{M}_w^A - \bar{M}_w^B) - W (\bar{M}_w^B - \bar{M}_w^A) \right] \]  
(2.2.13)
\[ Q = \sum_i W_i \delta W_i^2 \]
\[ = W (1 - W) \left( \bar{M}_w^A + \bar{M}_w^B - \bar{M}_w \right) \]  
(2.2.14)

since
\[ \frac{\bar{M}_w^A}{M_w} = \frac{1}{W} \sum_i W_i \frac{M_i}{M_w} \]  
(2.2.15)
\[
\frac{B}{M_w} = \frac{\sum c_i B M_i B}{\sum c_i B} = \frac{1}{1-W} \sum \gamma_i M_i (1-W_i)^2 \\
\frac{M_w}{M_w} = \frac{\sum c_i M_i}{\sum c_i} = \sum \gamma_i M_i
\] (2.2.16) (2.2.17)

The parameters \( P \) and \( Q \) are a useful way of expressing compositional heterogeneity; \( P \) is a measure of the molecular weight influence on compositional heterogeneity and \( Q \) is an overall measure of compositional drift.

If the quadratic equation 2.2.12 is plotted, it will have the form illustrated in Figure 2.2.1, on which some features of interest have been shown. For non-zero \( P \) and \( Q \) values, i.e. if the copolymer is heterogeneous in composition, the true \( M_w \) value will only be obtained at zero \((\nu_A - \nu_B)/\nu\). One can see that this can never practically be obtained unless the copolymer units are all isorefractive. To approach the true \( M_w \) value one must maximise the solution refractive index increment, in either a positive or negative direction.

Thus to obtain \( M_w \) values for compositionally heterogeneous copolymers one should obtain \( M^* \) values in at least three solvents having different refractive indices. Additional quantities \( M_w^A \) and \( M_w^B \), together with the \( P \) and \( Q \) parameters, could also be calculated if composition \( W \) were obtained. If a suitable difference in refractive index between the two components does not exist, this can be obtained by selective sorption in a mixed solvent system \( 50, 51 \). In this case dialysis equilibrium must be obtained between solution and solvent when taking refractive index increment measurements.

Errors involved in the calculation of compositional heterogeneity parameters have been investigated, together with the most desirable conditions for their determination \( 52-54 \). These include large refractive index differences in parent homopolymers (and
between different solvents) and a sufficiently heterogeneous copolymer to make readings meaningful. Vorlicek and Kratochvil\(^5\) have devised a nomogram to determine the feasibility of such determinations, including \(Q\) estimation using a single measurement (by choosing a solvent such that \(v\) is zero) or two measurements (assuming \(P = 0\)).

If the only quantity desired is \(\bar{M}_w\), and the copolymer is compositionally homogeneous (i.e., both \(P\) and \(Q\) are zero), then the copolymer may be treated as a normal homopolymer.

2.2.2. Mixtures of Homopolymers (or Homopolymer Blends)

The following expressions can be derived for homopolymer mixtures:\(^2\)\(^5\)

\[
P = W(1 - W) (\bar{M}_w^A - \bar{M}_w^B) \tag{2.2.18}
\]

\[
Q = W(1 - W) [(1 - W)\bar{M}_w^A + W \bar{M}_w^B] \tag{2.2.19}
\]

It is not easy to distinguish from the form of \(P\) and \(Q\) whether a solution contains copolymers or a mixture of homopolymers. However, for copolymers \(\bar{M}_w\) can be written in the form

\[
\bar{M}_w = W\bar{M}_w^A + (1 - W)\bar{M}_w^B + 2\sum_{i=1}^{\infty} W_i \bar{M}_w^{1 - W_i} \tag{2.2.20}
\]

In the case of a mixture of homopolymers, the third term will be zero. Therefore if

\[
\bar{M}_w > W\bar{M}_w^A + (1 - W)\bar{M}_w^B \tag{2.2.21}
\]

copolymer must be present.
2.2.3. Random Copolymers

Using the general rules for distribution of composition established by Stockmayer, it has been shown that random copolymers should give a zero $P$ coefficient. In the case of azeotropic copolymers the curve denoting the variation of $M^*$ should be effectively horizontal and linear for all molecular weights considered in practice.

2.2.4. Block Copolymers

Consider an AB block copolymer where there is no correlation between the molecular weights of the individual blocks. If $\Omega_j^A$ is the probability that the A-portion of the molecule has molecular weight $M_j^A$ and $\Omega_k^B$ is the probability that the B-portion has molecular weight $M_k^B$, then the probability that a molecule has molecular weight $M_j^A = M_k^B$ is $\Omega_j^A \Omega_k^B$. Using equations 2.2.13 and 2.2.14 the following expressions may be derived for $P$ and $Q$:

\[
P = \sum c_{jk} M_j^A M_k^B (W_j - W) / \sum c_{jk} M_j^A M_k^B
\]

\[
= \sum \Omega_j^A \Omega_k^B (M_j^A + M_k^B)^2 \left[ \frac{M_j^A}{M_j^A + M_k^B} - W \right] / \sum \Omega_j^A \Omega_k^B (M_j^A + M_k^B)^2
\]

\[
= W(1 - W)\left[ \frac{M_n^A}{M_n^A - (M_n^B - M_n^B)} \right]
\]

(2.2.22)

\[
Q = \sum \Omega_j^A \Omega_k^B (M_j^A + M_k^B)^2 \left[ \frac{M_j^A}{M_j^A + M_k^B} - W \right]^2 / \sum \Omega_j^A \Omega_k^B (M_j^A + M_k^B)^2
\]

\[
= W(1 - W)[(1 - W)(\frac{M_n^A}{M_n^A} - \frac{M_n^A}{M_n^B}) + W(\frac{M_n^B}{M_n^B} - \frac{M_n^B}{M_n^B})]
\]

(2.2.23)

Thus it can be seen that $Q$ is zero only when the sample is completely monodisperse, but $P$ will vanish when $\frac{M_n^A}{M_n^A} = \frac{M_n^B}{M_n^B}$. Equations 2.2.22 and 2.2.23 also hold for graft copolymers if the number and polydispersity of the branches are independent of the polydispersity of the chain formed from the other monomer.
More complex block copolymers may be treated using a similar model to that used in deriving equations 2.2.22 and 2.2.23.

A particular anomaly with block copolymers is the possibility of distorted Zimm plots. This occurs when the refractive index increment of one of the blocks is very small\textsuperscript{58,59} and has been attributed to intermolecular interference due to the large excluded volumes of the masked blocks. Not only is there a far stronger angular dependence, but also the possibility of a sharp downward curve in the $Kc/R_g$ against $c$ plot, even extrapolated to zero angle. Masking of blocks is considered a desirable technique, however, in determining the $M_A$ or $M_B$ values, and mixed solvents may be used for this purpose. A similar angular dependence has been noted for a polystyrene-polydimethylsiloxane block copolymer solution in toluene (giving one positive and one negative refractive index increment), although concentration dependence appears perfectly linear\textsuperscript{60}. 
Figure 2.2.1. $M^*$ drawn as a function of $(\nu_A - \nu_B)/\nu$.
See text for meaning of symbols.
Section 2.3

Gel Permeation Chromatography

GPC is a liquid chromatography technique capable of separating molecules according to their size in solution. Solvent is continuously pumped through a set of columns packed with porous gel particles. When a polymer solution is injected into the solvent stream it is eluted through the columns, where the molecular size sorting process takes place.

2.3.1. Separation Processes

Under normal GPC operating conditions, separation is now considered to be dominated by size exclusion mechanisms.\(^{61,62}\)

Since the sizes of the gel pores are of the same order of magnitude as those of the polymer molecules, more pore volume will be available to the smaller molecules than the larger ones, large enough molecules being totally excluded from the pores. Assuming diffusion processes into and out of the pores are fast when compared to solvent flow, molecules will tend to occupy all the volume available to them. Smaller molecules will therefore take longer to pass through the columns.

For a particular molecular species, this can be expressed mathematically as

\[
V_e = V_o + K_d V_I
\]  

(2.3.1)

where \(V_e\) is the peak elution volume, \(V_o\) the interstitial volume between the gel particles, \(V_I\) the volume of liquid within the pores, and \(K_d\) is the distribution function for the particular species, or the proportion of pore volume accessible to that species, i.e.

\[
K_d = \frac{V_{I,acc}}{V_I}
\]  

(2.3.2)
where \( V_{I, \text{acc}} \) is the accessible pore volume.

Earliest investigations used models \(^{63,64}\) which considered that molecules would have accessible to them the total pore volume of the pores into which they would fit (although Cantow and Johnson used a correction factor). Thus, for any molecular species, \( V_{I, \text{acc}} \) would be the total pore volume of the pores larger than the molecular size of that species. Separation of a range of molecular sizes would therefore require a similar range of pore sizes.

More separation will in fact be achieved than the above theory postulates, however, due to wall effects. Within a particular pore, a small molecule can occupy positions closer to the pore walls than can a large one. Thus more volume is accessible to smaller molecules and a separation of non-excluded species should occur even when all pore sizes are identical. This also implies that pore geometry as well as pore size is important. Models have been investigated for various pore geometries, the exclusion mechanism being considered as a reduction in conformational entropy of the molecules in pores of finite sizes \(^{65-67}\).

Complete separation by size exclusion would require equilibrium to be reached between the mobile phase occupying the interstitial volume and the stationary phase occupying the pores. If this is not achieved, separation by diffusion mechanisms can also occur \(^{68,69}\). Thus, because diffusion processes are slower for higher molecular weight species, large molecules are less likely to enter the stationary phase, and will be eluted through the columns faster. Such a mechanism will be flow rate dependent, but under normal operating conditions, its effect is not significant.

A further possible flow rate dependent mechanism could be separation by flow itself \(^{70}\), due to a combination of wall effects and the fact that flow velocity profiles exist. This is generally considered insignificant \(^{61}\).

Adsorption sometimes acts as a separation mechanism \(^{71}\).
It tends to withhold larger molecules so that, when it occurs, it will, if anything, oppose the dominant size exclusion mechanism, and decrease resolution.

2.3.2. Calculation of Molecular Weight Distributions

Since GPC is a secondary technique, column calibration is necessary for determination of molecular weight distributions (MWD's).

Usually several narrow MWD standards of known molecular weights are injected, and the elution volume (or elution time) of each peak determined. A similar set of data is sometimes obtained by injecting a single broad MWD standard whose complete MWD is known.

It is usually convenient to take the logarithm of the molecular weight, as this gives a fairly linear plot when plotted against elution volume over much of the calibration curve. The general shape of such a calibration plot is shown in Figure 2.3.1. Each elution volume therefore corresponds to a particular molecular weight of the calibrating polymer type.

To calculate the molecular weight of molecules of another polymer type eluted at the same volume, it is common practice to use a "universal calibration" procedure. This procedure assumes that separation takes place exclusively according to molecular size, so that, if the correct size parameter and its relationship to molecular weight can be found, the molecular weight of any polymer eluted at a particular volume can be calculated.

The size parameter most commonly used for such calculations is the hydrodynamic volume \( \eta M \), expressed in the form \( [\eta]M \), where \([\eta]\) is the intrinsic viscosity and \(M\) the molecular weight for the species considered. The relationship between \([\eta]\) and \(M\) is given by the Mark-Houwink-Sakurada equation:

\[
[\eta] = KM^a
\]
where $K$ and $a$ are the Mark-Houwink parameters. The hydrodynamic
volume $V_h$ can therefore be expressed in the form

$$V_h = KM^a + 1$$  \hspace{1cm} (2.3.4)

At any elution volume $V_h$ should be the same regardless of
polymer type. Since each elution volume has been assigned a cali-
bration molecular weight $M_{1i}$ corresponding to a particular polymer
type, the molecular weight $M_{2i}$ of a second polymer type eluting at
the same elution volume can be calculated according to the equation

$$K_2 M_{2i}^a + 1 = K_1 M_{1i}^a + 1$$  \hspace{1cm} (2.3.5)

where $K_1$ and $a_1$ are the Mark-Houwink parameters corresponding
to the calibration polymer type, and $K_2$ and $a_2$ are those for the
second polymer type.

A suggested improvement to such a calibration involves the
use of a modified expression for hydrodynamic volume $^{21}$, $[\eta]M/f$,
where $f$ can be reduced to a function of the Mark-Houwink parameter
$a$. Another size parameter sometimes used is the unperturbed
end-to-end distance of the polymer chains $^{22}$.

To obtain the full molecular weight distribution of a polymer
sample a reading from the concentration detector is taken at regular
elution volume intervals. The detector response $h_i$ will be propor-
tional to the weight fraction $Y_i$ at that elution volume:

$$Y_i = \frac{h_i}{\sum_{i} h_i}$$  \hspace{1cm} (2.3.6)

It is usual to plot weight fraction against log $M$. However,
since equal elution volume intervals do not necessarily correspond
to equal log $M$ intervals, it is necessary, strictly speaking, to
correct the $Y_i$ values by dividing by the calibration slope and
normalising $^{73}$.

Molecular weight averages may be calculated from the $Y_i$
values obtained from equation 2.3.6 and the calculated molecular weights \( M_i \) at each elution volume:

\[
\bar{M}_n = \frac{1}{\sum_i w_i/M_i}
\]

(2.3.7)

\[
\bar{M}_w = \sum_i w_i M_i
\]

(2.3.8)
Figure 2.3.1. A typical GPC column calibration.
Section 2.4

The Use of Low-Angle Laser Light Scattering with Gel Permeation Chromatography

It is not always possible to successfully apply universal calibration techniques to GPC chromatograms in order to obtain a true MWD. Although the methodology is applicable to most systems, Mark-Houwink parameters are seldom accurately known. A direct measurement of the molecular weight of the polymer molecules emerging from the GPC columns is therefore desirable. The most successful way of continuous molecular weight monitoring has been by use of low angle laser light scattering

2.4.1. Continuous Molecular Weight Monitoring in GPC/LALLS

The basic set-up of a GPC/LALLS system is shown in Figure 1. If a known weight of polymer is injected the molecular weight $M_i$ at the $i$th interval can be calculated by using the basic light scattering equation:

$$\frac{Kc_i}{R_{\theta_i}} = \frac{1}{M_i} + 2A_{2i}c_i$$

(2.4.1)

$R_{\theta_i}$ is the excess Rayleigh factor at the $i$th interval, and $A_{2i}$ is the second virial coefficient as applied to molecules of type $i$. The concentration $c_i$ of such molecules is calculated from the detector response as:

$$c_i = \frac{m}{\sum_i v_i} \frac{h_i}{\sum_i h_i}$$

(2.4.2)

where

$h_i = \text{detector reading},$

$v_i = \text{volume of effluent passing through the column during the } i\text{th interval},$

$m = \text{mass of sample injected.}$
$A_{2i}$ varies only slightly with molecular weight and is usually considered to be the second virial coefficient $A_2$ as determined from static LALLS measurements. Since its contribution is only around 1% to the final result, no large errors will result in ignoring it altogether when the correct value is not known.

From the above calculation of molecular weights $M_i$, the molecular weight distribution and the weight and number average molecular weights may be calculated.

2.4.2. Use of a Column Calibration in GPC/LALLS Calculations

The above calculations should give a correct value for the $\bar{M}_w$, but $\bar{M}_n$ values tend to be too high. At each elution volume it is the weight average molecular weight of the fraction which is actually being measured, and, due to imperfect resolution, the calculated $\bar{M}_n$ value will be raised.

Another problem occurs at each end of the chromatogram. Here molecular weight calculations are highly inaccurate due to a low detector response. In particular, at the low molecular weight end a signal may be significant as measured on the concentration detector but too small to detect on the LALLS detector.

A partial solution to both the above problems is to create a complete column calibration for each GPC/LALLS run from the LALLS $M_i$ values and their corresponding elution volumes, using a curve fitting technique. Such a calibration can then be used to analyse the whole chromatogram obtained from the concentration detector response.

Although the calibration curve shown in Figure 2.3.1 is far from linear overall, a single sample is likely to spread over only a relatively small portion of such a calibration. The approximation of a linear calibration over the range of the sample has therefore
been adopted for use in this laboratory, i.e.,

\[ \log M = aV + b \]  

(2.4.3)

where

- \( M \) = molecular weight
- \( V \) = elution volume

\( a \) and \( b \) are constants for the calibration.

If data are available for \( N \) calibration points, each having an equal weighting, a least squares analysis will give:

\[
\begin{align*}
a &= \frac{N \sum V_i \log M_i - \sum \log M_i}{N \sum V_i^2 - (\sum V_i)^2} \\
b &= \frac{\sum \log M_i \sum V_i^2 - \sum V_i \sum V_i \log M_i}{N \sum V_i^2 - (\sum V_i)^2}
\end{align*}
\]

(2.4.4)

(2.4.5)

where \( M_i \) and \( V_i \) are the molecular weight and elution volume values corresponding to the \( i \)th calibration point.

In the case of molecular weights calculated at regular intervals using an on-line LALLS detector, there will be a weighting of each due to both the LALLS detector response \( h_i \) and the concentration detector response \( x_i \). The weighting of each point is therefore \( h_i x_i \), and \( N \) will be replaced by \( \sum_i h_i x_i \):

\[
\begin{align*}
a &= \frac{\sum h_i x_i \log M_i - \sum h_i x_i v_i \sum h_i x_i \log M_i}{\sum h_i x_i v_i^2 - (\sum h_i x_i v_i)^2} \\
b &= \frac{\sum h_i x_i \log M_i \sum h_i x_i v_i^2 - \sum h_i x_i v_i \sum h_i x_i v_i \log M_i}{\sum h_i v_i \sum h_i x_i v_i^2 - (\sum h_i x_i v_i)^2}
\end{align*}
\]

(2.4.6)

(2.4.7)

GPC/LALLS overestimates \( M_i \) values at the lower
molecular weight end of the chromatogram due to imperfect column resolution. This causes an error in the slope of the type of calibration described above. The use of such a calibration does, however, avoid the derivation of highly inaccurate molecular weight values at the ends of the chromatogram (due to both imperfect column resolution and low detector responses). It therefore gives a better picture of the MWD than can be obtained without employing a computational technique of this type.

The type of calibration described above should be most accurate near the centre of the calibration curve, i.e., where both detectors have a fairly high response. The elution volume corresponding to the $\bar{M}_w$ of a sample should fall within this region, and since the $\bar{M}_w$ value itself can also be accurately determined using GPC/LALLS, the technique can be used to provide a complete column calibration for a particular polymer type. Thus, by running a series of samples, several $\bar{M}_w$ values and their corresponding elution volumes can be calculated. These could then be used in a full column calibration.
Section 2.5

The Use of Dual Detector Gel Permeation Chromatography for Copolymer Characterisation

The use of two concentration detectors in a GPC chromatograph has been used for some time for characterising two component copolymers. With such a system, information on copolymer composition may be obtained at each elution volume. If a spectroscopic detector is used, two GPC runs using two different detector wavelengths may achieve the same effect.

2.5.1. Copolymer Composition

It is usual to make the following assumptions when determining composition using the dual detector system:

(a) Each detector has a linear response with respect to concentration.

(b) Response is independent of molecular weight.

(c) Each component of a copolymer will contribute to the detector response an amount equal to the same concentration of homopolymer.

In the case of a GPC system used to investigate a copolymer having components labelled A and B, four detector calibration constants are obtained by using both the responses from known concentrations of homopolymers A and B. In the separation of the copolymer, the response of each detector is the sum of the responses due to each component:

\[ r_{1i} = k_{A1} c_{Ai} + k_{B1} c_{Bi} \]  \hspace{1cm} (2.5.1)

\[ r_{2i} = k_{A2} c_{Ai} + k_{B2} c_{Bi} \]  \hspace{1cm} (2.5.2)

where \( c_{Ai} \) and \( c_{Bi} \) are concentrations of each component at elution
volume interval \( i \), \( r_{1i} \) and \( r_{2i} \) are the two detector responses, and
\( k_{A1} \), \( k_{A2} \), \( k_{B1} \), and \( k_{B2} \) are the detector calibration constants.

Combining equations 2.5.1 and 2.5.2 gives

\[
\frac{r_{1i} k_{B2} - r_{2i} k_{B1}}{k_{A1} k_{B2} - k_{A2} k_{B1}}
\]

(2.5.3)

\[
\frac{r_{2i} k_{A1} - r_{1i} k_{A2}}{k_{A1} k_{B2} - k_{A2} k_{B1}}
\]

(2.5.4)

From these concentrations, the average composition \( W_i \) can be obtained at each elution volume:

\[
W_i = \frac{c_{Ai}}{c_{Ai} + c_{Bi}}
\]

(2.5.5)

This type of analysis can be expected to hold true in most cases. However, at low molecular weights, detector response is likely to be molecular weight dependent, especially in the case of a refractive index detector. Also, in the case of copolymers having short sequence lengths, equations 2.5.1 and 2.5.2 are less likely to hold true. This problem is especially noticeable when an ultraviolet spectrophotometer is used as a detector.

2.5.2. Copolymer Molecular Weights

Any column calibration in terms of copolymer molecular weight is likely to be unique to a particular copolymer composition. Since a range of compositions may be present at each elution volume, a range of molecular weights is also likely. The dual detector technique only allows the assignment of a single value, however. It is sometimes sufficient to express such a value in terms of some homopolymer equivalent, but it is also possible to derive a more correct average value from composition data or to take a direct measurement using an on-line molecular weight detector.
Molecular weight derivations make use of the average composition at a particular elution volume, as determined above. Runyon et al.\textsuperscript{28} used an interpolation between the component homopolymer calibrations:

$$\log M_i = W_i \log M_{Ai} + (1-W_i) \log M_{Bi}$$ \hspace{1cm} (2, 5, 6)

where $M_i$ is the calculated copolymer molecular weight at the $i$th elution volume interval, and $M_{Ai}$ and $M_{Bi}$ are the homopolymer molecular weights which would be eluted at that interval. Such a calculation works well for linear copolymers so long as interactions between the copolymer components do not significantly distort the overall copolymer. It does not generally work well for random copolymers, therefore, due to the large number of heterocontacts.

An on-line viscometer\textsuperscript{35} is sometimes used together with the universal calibration assumption that copolymer molecules are fractionated according to hydrodynamic volume $[\eta]M$. Thus a copolymer molecular weight value can be obtained at each elution volume by comparison with an initial homopolymer calibration. This gets over the problem of interactions between the components. Tung\textsuperscript{34} has shown, however, that, in the case of block copolymers, there is likely to be a greater error in the viscometer measurements than in the assumptions made in equation 2.5.6. This is even more true when using high performance column technology involving relatively small elution volumes.

Some workers have used a combination of universal calibration and interpolation procedures, assuming knowledge of the appropriate parameters for each component homopolymer\textsuperscript{31,84,85}. Any calculation involving universal calibration techniques assumes no interaction between the sample polymer and the packing, so that separate homopolymer calibrations are likely to produce more accurate results. This is also a limitation to the on-line viscometer calibration\textsuperscript{82}.
Section 2.6

The Use of Low-Angle Laser Light Scattering with Dual Concentration Detector Gel Permeation Chromatography for Copolymer Characterisation

Only in exceptional circumstances should a LALLS photometer, used as an on-line GPC detector, yield a true molecular weight value for copolymers, for the reasons outlined in Section 2.2.

The purpose of this study is to use the difference between the apparent molecular weight, measured by LALLS, and that anticipated from dual detector GPC at each elution volume to estimate copolymer heterogeneity. In order to obtain the GPC values of the molecular weight two homopolymer column calibrations are obtained in the manner described in Subsection 2.4.2, using GPC/LALLS. Equation 2.5.6 can then be used at each elution volume.

The method of calculation described in this Section has been devised for use in this study.

2.6.1. Distributions Within Each GPC Fraction

A possible distribution of molecular weights and compositions is shown in Figure 2.6.1. Contour lines are used to show equal concentrations of molecules of a particular molecular weight-composition combination.

It can be seen that elution volume does not directly correspond to molecular weight. Composition is also involved, all three quantities being interrelated. At a typical elution volume $V_i$, all species along line PQ will be present. The fact that PQ is drawn as a straight line is a restatement of equation 2.5.6, and should generally approximate to the case for block copolymers. Line XY shows the composition calculated at each elution volume. At elution volume $V_i$, the calculated composition is $W_i$, $M_i$ being the molecular weight calculated according to equation 2.5.6.
$W_i$ is calculated according to equation 2.5.5. This can be re-expressed as:

$$W_i = \frac{\sum W_{ij} c_{ij}}{\sum c_{ij}}$$

$$= \sum W_{ij} \gamma_{ij}$$

(2.6.1)

where $W_{ij}$ is the composition, $c_{ij}$ the concentration, and $\gamma_{ij}$ the weight fraction of molecules of type $j$ in the $i$th fraction.

$W_i$ is therefore the weight average value of the composition, taking the same form as equation 2.2.17. It can be seen from Figure 2.6.1 that the shape of the log $M_{ij}$ distribution should be the same as that of the $W_{ij}$ distribution over species at elution volume $V_i$. Thus the log $M_i$ value, calculated according to equation 2.5.6, should also be a weight average value:

$$\log M_i = \sum \gamma_{ij} \log M_{ij}$$

(2.6.2)

The value of $M_i$ thus produced is expected to fall between the number and weight average molecular weights over the fraction.

The GPC/LALLS analysis described here assumes a weight average value for $M_i$. This is based on the principle that the MWD at each elution volume should be narrow. This assumption is fairly fundamental to the analysis.

2.6.2. Calculation of Apparent Molecular Weight Values at each Elution Volume by GPC/LALLS

An apparent molecular weight $M_{i*}$ can be calculated at each elution volume using equation 2.4.1, which becomes:

$$\frac{K_{c_i}}{R_{9i}} = \frac{1}{M_{i*}} + 2A_{2i} c_i$$

(2.6.3)
where \( K_i \) is the polymer constant, \( R_{si} \) the excess Rayleigh factor, \( A_{2i} \) the second virial coefficient, and \( c_i \) the overall concentration at the \( i \)th interval.

\[ K_i = K^* \nu_i^2 \]

(2.6.4)

where

\[ K^* = \frac{2\pi n_o^2}{N \lambda} (1 + \cos^2 \theta) \]

using the symbols defined in Section 2.1. \( \nu_i \) is the refractive index increment at elution volume \( V_i \), and can be calculated according to equation 2.2.9, which becomes

\[ \nu_i = W_i \nu_A + (1 - W_i) \nu_B \]

(2.6.5)

where \( \nu_A \) and \( \nu_B \) are the refractive index increments of the A and B units respectively. \( K_i \) can therefore be calculated at any elution volume.

\( A_{2i} \) is also composition dependent, but there is not a straightforward relationship to \( W_i \). Since its contribution to the overall result is small, however, it can be reasonably ignored.

2.6.3. Calculation of Compositional Heterogeneity at each Elution Volume

From the above it is possible to calculate two values for the molecular weight at each elution volume. The \( M_i \) value is obtained from a dual column calibration using homopolymers, and the \( M_i^* \) value is obtained from the GPC/LALLS results.

In Section 2.2, equation 2.2.12 related the weight average molecular weight \( M_w \) of a copolymer to its apparent molecular weight \( M^* \) as follows:

\[ M^* - M_w = 2P \left( \frac{\nu_A - \nu_B}{\nu} \right) + Q \left( \frac{\nu_A - \nu_B}{\nu} \right)^2 \]
where the symbols have the meanings given in Section 2.2.

If a narrow MWD exists within the elution volume fraction, $M_i$ can be considered to be the weight average value. Therefore:

$$M_i^* - M_i = 2P_i \left( \frac{\varphi_A - \varphi_B}{\varphi_i} \right) + Q_i \left( \frac{\varphi_A - \varphi_B}{\varphi_i} \right)^2$$

(2.6.6)

where $P_i$ and $Q_i$ are the heterogeneity parameters of the $i$th fraction.

In the case of a narrow MWD, and a large value for $(\varphi_A - \varphi_B)/\varphi_i$, one can ignore the first term on the right hand side of equation 2.6.6, which then becomes:

$$M_i^* - M_i = Q_i \left( \frac{\varphi_A - \varphi_B}{\varphi_i} \right)^2$$

(2.6.7)

Enough information exists, therefore, to allow the calculation of $Q_i$.

The maximum possible value of $Q_i$ would be that obtained when the fraction at $V_i$ contained only a mixture of homopolymers. The value of $Q$ for a homopolymer mixture is given by equation 2.2.19:

$$Q = W(1-W)[(1-W)\overline{M_w}^A + W\overline{M_w}^B]$$

In the case of a single fraction, $\overline{M_w}^A$ and $\overline{M_w}^B$ can be replaced by the two homopolymer calibration values $M_{A_i}$ and $M_{B_i}$, shown on Figure 2.6.1. The maximum value of $Q_i$ is therefore:

$$Q_{i, max} = W_i(1-W_i)[(1-W_i)M_{A_i} + W_iM_{B_i}]$$

(2.6.8)

The heterogeneity can thus usefully be expressed as:

$$H_i = \frac{Q_i}{Q_{i, max}}$$

(2.6.9)

$H_i$ may vary from a value of zero for a compositionally homogeneous copolymer to a value of 1 for a homopolymer blend.
2.6.4 Calculation of Overall Parameters

The component weight average molecular weights can, from equations 2.2.13 and 2.2.14, be expressed as:

\[
\overline{M}_w^A = W M_w + \frac{Q}{W} - 2P \quad (2.6.10)
\]

\[
\overline{M}_w^B = (1-W)M_w + \frac{Q}{(1-W)} + 2P \quad (2.6.11)
\]

Making the assumption that \( P_i \rightarrow 0 \) for the narrow MWD's of single fractions, one obtains:

\[
\overline{M}_{w_i}^A = W_i M_{i,1} + \frac{\Omega_i}{W_i} \quad (2.6.12)
\]

\[
\overline{M}_{w_i}^B = (1-W_i)M_{i,1} + \frac{\Omega_i}{(1-W_i)} \quad (2.6.13)
\]

Number average molecular weights for copolymer components can be calculated as:

\[
\overline{M}_n^A = W M_n \quad (2.6.14)
\]

\[
\overline{M}_n^B = (1-W)M_n \quad (2.6.15)
\]

where \( \overline{M}_n \) is the number average molecular weight of the copolymer. At each elution volume this is taken as equal to \( M_i \):

\[
\overline{M}_{n_i}^A = W_i M_i \quad (2.6.16)
\]

\[
\overline{M}_{n_i}^B = (1-W_i)M_i \quad (2.6.17)
\]

A weight average quantity can be obtained by weight averaging quantities which are already in a weight average form. Therefore, from equations 2.2.15 and 2.2.16:

\[
\overline{M}_w^A = \frac{\sum c_{iA} \overline{M}_{w_i}^A}{\sum c_{iA}} \quad (2.6.18)
\]
\[ \overline{M_B} = \frac{\sum c_i B}{\sum i} \]

where \( c_{iA} \) and \( c_{iB} \) are the concentrations of each component calculated at each elution volume.

\( \overline{M_B} \) can be calculated from equation 2.3.8, and equation 2.3.7 can be used to calculate \( \overline{M_n} \). The overall composition \( W \), calculated as \( \frac{\sum c_{iA}}{\sum c_i} \), is used in equations 2.6.14 and 2.6.15 to evaluate \( \overline{M_n} \) and \( \overline{M_n} \).

Values of \( P \) and \( Q \) can be obtained from equations 2.2.13 and 2.2.14. The maximum possible value of \( Q \), \( Q_{\text{max}} \), calculated according to equation 2.2.19, may be used in estimating overall heterogeneity \( H \):

\[ H = \frac{Q}{Q_{\text{max}}} \]  

This should strictly speaking be more correct than the method of obtaining \( Q/Q_{\text{max}} \) used by Jordan, who used a value of \( Q_{\text{max}} \) calculated as \( W(1-W)M_w \).
Figure 2.6.1. Contour map showing the possible molecular weight and composition distributions of a copolymer. Molecular weight and composition distributions are shown individually for all species along line PQ, representing an elution volume $V_i$ in a GPC experiment. See text for a complete explanation.
CHAPTER 3

EXPERIMENTAL
Section 3.1

Determination of Refractive Index Increments

3.1.1. Instrumental

A Chromatix KMX16 laser differential refractometer was used for all measurements. Its basic structure is illustrated in Figure 3.1.1.

The laser beam passes through both the reference and sample halves of a sample cell, through an angle multiplier and then reflected off a mirror. The mirror can be rotated by means of a handwheel until the beam returns along its original path. When this occurs a null reading is obtained on the meter. The cell can be turned through 180°, and a null reading again obtained after a suitable rotation of the mirror. The extent of mirror rotation required between these two null positions can be calibrated against refractive index differences between the contents of two cell halves.

The cell and its surrounding mantle contain heating elements. The temperature of both is accurately controlled by means of electronic circuitry.

3.1.2. Experimental Method

For each determination, five solutions in the concentration range $4 \times 10^{-3} \text{ g cm}^{-3}$ to $2 \times 10^{-2} \text{ g cm}^{-3}$ were made up separately. The polymer was weighed out and a little solvent added the day before running. The solution was made up to the mark in a volumetric flask at least half an hour before running.

With solvent in the reference side of the cell, the necessary mirror rotation between the two null points was measured for solvent and each solution, in turn, in the sample side (the solvent reading is necessary so that any slight irregularities in the cell geometry can be accounted for when solution readings are taken). A value of excess refractive index of solution over solvent, Δn,
could therefore be calculated for each solution, making use of a
calibration previously obtained using a series of sodium chloride
solutions.

Both solvent and solutions were left in the cell for 40 minutes
before taking any readings, to allow a steady temperature to be
reached. The cell was agitated after 20 minutes. The instrument
was left for one minute after each 180° rotation of the cell before
taking a reading. At least two readings were taken for each concen-
tration.

3.1.3. Calculation of Refractive Index Increments

The value of $\Delta n/c$ was calculated at each concentration $c$. The
required refractive index increment is the infinite dilution limit of
$\Delta n/c$. However, for all situations in this study, any variation in
$\Delta n/c$ with concentration was less than the experimental error,
which increases with decreasing concentration. A mean value of
$\Delta n/c$ over the concentration range was therefore used in preference
to an extrapolation to zero concentration.
Figure 3.1.1. Basic structure of the Chromatix KMX16 laser differential refractometer.
Section 3.2

"Static" Low Angle Laser Light Scattering Measurements

3.2.1. Instrumental

A Chromatix KMX6 LALLS photometer, as shown in Figure 1.1.1, was used for all measurements.

A 15mm polytetrafluoroethylene cell was used, sandwiched between two silica windows.

Rayleigh factor \( R_e \) values were obtained by comparing scattered intensity \( I_e \) with straight through intensity (which can be considered to be the same as the incident intensity \( I_o \)). Because \( I_o \) is much greater than \( I_e \), a series of attenuators was inserted in the incident beam when measuring \( I_o \), to allow comparable readings. Then

\[
R_e = \frac{G_e}{G_o} \times (\sigma' t')^{-1} \times D
\]

(3.2.1)

where \( G_e \) and \( G_o \) are the instrument readings for the scattered and straight through light respectively, \( D \) is a constant to account for the attenuation on measuring \( G_o \), \( \sigma' \) is the effective solid angle, and \( t' \) the equivalent path length. \( \sigma' \) depends mainly on the annulus used on measuring \( G_e \), but the effect of refraction by the solution and the cell windows must also be taken into account. \( t' \) depends on these quantities, but also on the size of the field stop aperture.

All \( G_e \) measurements were taken with the 6-7° annulus in the beam. A 3s instrumental time constant and a 0.2mm field stop aperture were used for all measurements.

3.2.2. Solution Preparation and Introduction

For each determination, four solutions were prepared separately, as described in Subsection 3.1.2. The concentration range was dependent on the refractive index increment for the particular solution type.
Solution filtration was achieved by use of a prefilter and a membrane filter connected in line with the sample cell. The prefilter consisted of a short length of chromatography column containing chromatographic glass granules and the membrane filter used was polyethylene backed polytetrafluoroethylene (PTFE) containing 0.2 μm pores.

All readings were made with solution flowing through the sample cell at about 1 cm min⁻¹. This was achieved by using a syringe pump. A total of about 20 cm³ of each solution was passed through the cell to ensure that the correct concentration had been reached.

3.2.3. Molecular Weight Determination

Rayleigh factors were measured for the solvent and each of the four solutions.

Excess Rayleigh ($\overline{R}_q$) values were obtained by subtracting the solvent Rayleigh factor from each solution value.

Molecular weight values were obtained by performing a least squares calculation on the results from the four solutions, using equation 2.1.16.

3.2.4. Accuracy of Measured Molecular Weights

An inter-laboratory round-robin experiment has been conducted to assess the reproducibility of LALLS $\overline{M}_w$ measurements, as performed on toluene solutions of a broad molecular weight polystyrene. A duplicate run on each of four samples was asked of each laboratory. The measured $\overline{M}_w$ results are summarised in Table 3.2.1.

The samples were all nominally the same, obtained from a single batch through a sample splitting process. However, laboratory 1 was able to show a significant difference between their
molecular weights. Laboratories 2, 3, 4 and 5 formed a statistically homogeneous group, considered in terms of within laboratory variation. The standard deviation in measured $M_w$ over the eight runs performed by each of these laboratories is shown in Table 3.2.1. However, measured toluene Rayleigh factors obtained by these laboratories showed that at least three of them were using instruments in need of adjustment. This situation has since been corrected.

Overall there is good agreement between laboratories, despite the instrumental faults mentioned above. The ability of laboratory 1 to differentiate between samples obtained in this way has not been observed using other techniques.
<table>
<thead>
<tr>
<th></th>
<th>Laboratory 1</th>
<th>Laboratory 2</th>
<th>Laboratory 3</th>
<th>Laboratory 4</th>
<th>Laboratory 5</th>
<th>Laboratory 6</th>
</tr>
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<td>Sample A</td>
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<td>292,000</td>
<td>342,000</td>
<td>357,000</td>
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<td>331,000</td>
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<td>333,000</td>
<td>354,000</td>
<td>339,000</td>
<td>299,000</td>
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<td>351,000</td>
<td>305,000</td>
<td>335,000</td>
</tr>
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<td>331,000</td>
<td>358,000</td>
<td>302,000</td>
<td>319,000</td>
</tr>
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<td>343,000</td>
<td>308,000</td>
<td>384,000</td>
</tr>
<tr>
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<td>313,000</td>
<td>374,000</td>
<td>344,000</td>
<td>408,000</td>
</tr>
<tr>
<td>Sample D</td>
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<td>321,000</td>
<td>359,000</td>
<td>301,000</td>
<td>314,000</td>
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<td>Standard Deviation</td>
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<td>11,000</td>
<td>9,000</td>
<td>17,000</td>
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</tr>
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<td>Run Temperature</td>
<td>25</td>
<td>24-27</td>
<td>21.5-24.5</td>
<td>~23</td>
<td>23</td>
<td>23-25.5</td>
</tr>
<tr>
<td>(°C)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \nu ) (cm(^3)g(^{-1}))</td>
<td>0.112</td>
<td>0.110</td>
<td>0.107</td>
<td>0.107</td>
<td>0.110</td>
<td>0.110</td>
</tr>
</tbody>
</table>

**Table 3.2.1**: LALLS \( \overline{M}_w \) data obtained from an inter-laboratory round-robin experiment. Also shown are the standard deviations over 8 runs, the run temperatures, and the refractive index increment values \( \nu \) used in calculating the \( \overline{M}_w \) values.
Section 3.3

Viscometric Determinations

All viscometry measurements were performed using an Ubbelohde viscometer, as shown in Figure 3.3.1. The temperature of the viscometer was maintained at 25.2 ± 0.05°C in a water bath.

For each determination, 25 cm$^3$ of stock solution was made up in a volumetric flask, according to the method of Subsection 3.1.2, at a concentration dependent on molecular weight. The solvent and stock solutions were filtered through a glass sinter before use, and kept at the run temperature for at least ten minutes. Timings were made for solvent to fall through the viscometer capillary, followed by timings for each solution, prepared by successive dilutions of the stock solution in the viscometer. Reproducibility of within 0.2 s was normally looked for. In the cases when solution times were less than 20 s different from solvent times reproducibility of within 0.1 s was looked for.

The results of $(t-t_o)/t_o c$ and $\ln (t/t_o)/c$ were plotted against concentration $c$, where $t$ and $t_o$ are the solution and solvent times respectively. Such a plot is shown in Figure 3.3.2. The intrinsic viscosity was obtained by extrapolating both lines to zero concentration, and choosing the best common intercept.
Figure 3.3.1. An Ubbelohde viscometer.
Figure 3.3.2. Example of a graph used to find the intrinsic viscosity of a sample.

Sample: PS2
Solvent: Chloroform
Temperature: 25.2°C
Section 3.4

Gel Permeation Chromatography

3.4.1. Instrumental

A steady stream of solvent was pumped, using a Dupont 870 chromatographic pump, through a Specac 3.100 injection valve having a 0.25 cm$^3$ loop, followed by an inline mobile phase depth filter and four PL gel 30 cm columns, maintained at a temperature of 80°C.

The column packing consisted of highly porous 10 μm poly(styrene/vinylbenzene) spherical particles. Columns having packings with quoted pore size of $10^3$ Å, $10^4$ Å, $10^5$ Å, and $10^6$ Å were used.

The solvent flow was passed from the columns through a series of detectors. A Wilks Miran-1A variable filter infrared (IR) spectrometer was used fitted with a 1.5mm path length ultra-micro flow-through cell with calcium fluoride windows. A Waters R401 differential refractometer (RI detector) was used as a second concentration detector, connected as the last detector in line. A Chromatix KMX-6 LALLS photometer was fitted with a 4.93mm flow through cell for in line light scattering measurements. A low volume in line mobile phase depth filter and a 0.2 μm PTFE in line membrane filter were installed immediately prior to the LALLS photometer to remove any dust that could interfere with the LALLS signal. All detector outputs were fed to chart recorders.

A Phase Separations liquid flowmeter was used as the last component in line for some of the runs.

A diagram of the complete set up is shown in Figure 3.4.1 although not all the components shown were used for all the runs.

Instrument settings are shown in Table 3.4.1.
3.4.2. Selection of Concentration Detector/Solvent System

During the earlier stages of the project there was no RI detector available so two separate runs at two separate IR wavelengths had to be performed on each copolymer. Tetrachloroethylene was chosen as the solvent because it had suitable IR windows for detecting both components of the polystyrene/polydimethylsiloxane (PS/PDMS) copolymers used in this investigation. At a wavelength of 3.42 μm, the detector should respond mainly to the PS component, and at a wavelength of 9.45 μm it should respond mainly to the PDMS component.

GPC only (i.e. without LALLS) runs were performed on the copolymers using this system, but spurious peaks frequently occurred on chromatograms obtained when the detector was set at 3.42 μm (see Figure 3.4.2). It was necessary to ignore any signal occurring after a time of 36 min. When the RI detector became available, therefore, this was used in combination with the IR detector set at 9.45 μm, rather than use the IR detector twice. The results obtained using double IR runs have been retained only for comparison with the RI/IR results, and for use in investigating the relationship between refractive increments and copolymer composition.

3.4.3. Solution Preparation

All solutions were made up according to the method described in Subsection 3.1.2, except that each solution contained 0.1% of toluene. This acted as an internal marker, whose elution time was used to correct for any variations in flow rate between runs. An average marker elution time for a 1 cm³ min⁻¹ flow rate was calculated with the help of the flow meter. All elution times were then corrected to their value at this flow rate, making use of the marker peak position.

Other than those used in the various calibrations, all...
solutions were made up to a concentration of about $5 \times 10^{-3} \text{ g cm}^{-3}$. Figure 3.4.3 shows the effect of solution concentration on calculated GPC weight average molecular weights. All the samples used in this study had a molecular weight of around 50,000. The figure shows all results to be effectively independent of concentration for this molecular weight at the concentration used.

Narrow MWD polystyrene standards were run at a concentration of $5 \times 10^{-4} \text{ g cm}^{-3}$. The solution concentrations used for GPC/LALLS column calibrations were dependent on molecular weight.

All solutions were filtered through a 0.45 µm polyamide membrane filter immediately before injection.

3.4.4. GPC Run Technique

With the injection valve in its load position, the sample loop was flushed with 2 cm$^3$ of solvent, then 2 cm$^3$ of air, 0.5 cm$^3$ of solution, and a further 2 cm$^3$ of air. Then 1 cm$^3$ of solution was used to fill the loop. The injection valve was turned to its inject position, and the chart recorders switched on immediately.

When the LALLS photometer was being used, chart recorder traces for zero signal and for $G_o$ were taken near the start of the run (see equation 3.2.1). The $G_o$ value used was the difference between the heights of these two chart recorder traces. When scattered light readings were being made (i.e. during the chromatogram) the zero offset on the LALLS photometer was used. The settings are shown in Table 3.4.1.

Baselines were drawn manually on the chart recorder traces, and peak heights measured at 30s intervals using a ruler. This information was processed on an IBM System 34 mainframe computer.
Figure 3.4.1. GPC set up used for this work.
Figure 3.4.2. Example of a copolymer GPC trace obtained from the IR detector set at 3.42 μm, showing the presence of a spurious peak.

Sample: B16
Solvent: TTCE
Flow Rate: 1 cm³ min⁻¹
Column temperature: 80°C
The effect of injected polymer concentration on the $M_w$ values obtained from GPC results for PS and PDMS homopolymers.

Solvent: TTCE
Flow rate: 1 cm$^3$ min$^{-1}$
Column temperature: 80°C
Loop size: 0.25 cm$^3$
PUMP
Flow rate \( a \): 1 cm\(^3\) min\(^{-1}\)

RI DETECTOR
Sensitivity: 4 \( b \)

IR DETECTOR
Sensitivity: 0.25 A\(^c\)
Wavelength: 9.45 µm\(^d\)
Meter response: 40 s
Slit width: 2 mm

LALLS DETECTOR
Sensitivity\(^e\): 800
Instrumental time constant: 1 s or 10 s\(^f\)
Annulus: 6°-7°
Attenuators used during G\(_0\) measurement: 1, 3, 4

NOTES:

a. As set according to the dial on the pump.

b. For some GPC/LALLS column calibration runs, lower sensitivity settings were used.

c. For some of the higher concentration PDMS runs, a sensitivity of 1A was used. A setting of 0.1A was used for PS runs.

d. 3.42 µm was also used for some of the earlier runs (see text).

e. Instrument meter reading for solvent scatter. The 1V output was connected to a chart recorder set at sensitivity 0.2V to give a large signal.

f. Dependent on the behaviour of the chart recorder signal for solvent scatter. Account was taken of the set time constant during computation.

Table 3.4.1: GPC Instrument Settings.
Section 3.5

Materials Used

The PS/PDMS block copolymers were those previously prepared by G. Taylor \(^{89,90}\), at Loughborough University of Technology, by polymerising hexamethylcyclotrisiloxane onto polystyryllithium blocks using living anionic processes. A summary of the molecular weight and composition data obtained by Taylor, using GPC and silicon analysis, is shown in Table 3.5.1.

The narrow MWD PS standards used for column calibrations were obtained commercially from Polymer Laboratories.

All other homopolymers were samples received by the Polymer Supply and Characterisation Centre for characterisation. A summary of the GPC data originally obtained for these samples is given in Table 3.5.2.

All solvents were BDH General Purpose Reagents, except that Analar grade chloroform was used for viscometry work, and redistilled tetrachloroethylene was used during GPC/LALLS column calibrations.
<table>
<thead>
<tr>
<th>Copolymer</th>
<th>$\bar{M}_n^{PS}$ (a)</th>
<th>$\bar{M}_w/\bar{M}_n$ (b)</th>
<th>% PS (c)</th>
<th>$\bar{M}_n$ (d)</th>
<th>$\bar{M}_w$ (d)</th>
</tr>
</thead>
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<td>B12</td>
<td>45,700</td>
<td>1.31</td>
<td>61.6</td>
<td>74,000</td>
<td>96,900</td>
</tr>
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<td>B13</td>
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<td>1.43</td>
<td>42.9</td>
<td>106,500</td>
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<td>70.8</td>
<td>47,200</td>
<td>53,800</td>
</tr>
</tbody>
</table>

Notes:  

a) Obtained from GPC on polystyryllithium blocks prior to copolymerisation.  
b) Obtained from GPC on overall copolymer.  
c) Obtained from silicon analysis.  
d) Derived from data in other columns.

Table 3.5.1: Summary of the molecular weight and composition data obtained by Taylor for the copolymers used in this study.
<table>
<thead>
<tr>
<th>Sample</th>
<th>Polymer Type</th>
<th>$\bar{M}_n$</th>
<th>$\bar{M}_w$</th>
<th>$\frac{\bar{M}_w}{\bar{M}_n}$</th>
</tr>
</thead>
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<tr>
<td>APS5T</td>
<td>PS</td>
<td>10,200</td>
<td>49,700</td>
<td>4.89</td>
</tr>
<tr>
<td>APS6T</td>
<td>PS</td>
<td>8,600</td>
<td>47,200</td>
<td>5.30</td>
</tr>
<tr>
<td>APS10T</td>
<td>PS</td>
<td>4,600</td>
<td>18,100</td>
<td>3.95</td>
</tr>
<tr>
<td>APS11T</td>
<td>PS</td>
<td>13,400</td>
<td>77,700</td>
<td>5.80</td>
</tr>
<tr>
<td>RAFFP/39-12</td>
<td>PS</td>
<td>36,600</td>
<td>119,700</td>
<td>3.27</td>
</tr>
<tr>
<td>PS2</td>
<td>PS</td>
<td>102,600</td>
<td>265,900</td>
<td>2.59</td>
</tr>
<tr>
<td>PD10</td>
<td>PDMS</td>
<td>4,400</td>
<td>7,700</td>
<td>1.75</td>
</tr>
<tr>
<td>PD13</td>
<td>PDMS</td>
<td>6,500</td>
<td>12,000</td>
<td>1.86</td>
</tr>
<tr>
<td>PD14</td>
<td>PDMS</td>
<td>12,400</td>
<td>30,700</td>
<td>2.47</td>
</tr>
<tr>
<td>PD15</td>
<td>PDMS</td>
<td>18,800</td>
<td>44,200</td>
<td>2.35</td>
</tr>
<tr>
<td>PD16</td>
<td>PDMS</td>
<td>16,500</td>
<td>41,900</td>
<td>2.54</td>
</tr>
<tr>
<td>PD17</td>
<td>PDMS</td>
<td>18,000</td>
<td>39,800</td>
<td>2.22</td>
</tr>
<tr>
<td>PD18</td>
<td>PDMS</td>
<td>29,100</td>
<td>94,500</td>
<td>3.24</td>
</tr>
<tr>
<td>PD20</td>
<td>PDMS</td>
<td>32,600</td>
<td>123,400</td>
<td>3.78</td>
</tr>
<tr>
<td>PD23</td>
<td>PDMS</td>
<td>40,100</td>
<td>189,500</td>
<td>4.73</td>
</tr>
</tbody>
</table>

Table 3.5.2: Summary of the GPC results previously obtained for the homopolymers used in this study.
CHAPTER 4

RESULTS

AND

INTERPRETATION
Section 4.1

Refractive Index Increments

4.1.1. Aims of Section

1. To determine values of refractive index increments for use in light scattering calculations.

2. To check on the linear relationship between refractive index increments and composition for blends and copolymers, i.e., equation 2.2.9:

   \[ \nu = W \nu_A + (1-W) \nu_B \]

   This assumption is implicit both in copolymer light scattering calculations and in any dual concentration detector GPC which makes use of an RI detector.

3. To check on any appreciable variation in refractive index increments with molecular weight. Such a variation would distort any GPC trace from an RI detector, interfering with dual concentration detector composition calculations. It would also affect molecular weights calculated from light scattering (especially affecting molecular weight distributions calculated using GPC/LALLS).

4.1.2. Homopolymer Results

The results obtained for representative PS and PDMS homopolymers for the molecular weight range considered here are shown in Table 4.1.1.
4.1.3. Variation of Refractive Index Increments with Composition

A single copolymer sample (B21) and a blend (a mixture of homopolymers APS5T and PD17) were used to test the relationship given by equation 2.2.9. This equation was used to calculate theoretical values for refractive index increments, and these values were compared with those measured. The results are shown in Table 4.1.2. For the calculation of the theoretical values, the homopolymer values determined in Subsection 4.1.2 were used. The copolymer composition used in the calculation was 31.47% PS. This value was that obtained from GPC using two IR runs (see Subsection 3.4.2). The composition of the blend, from the mass of homopolymers initially weighed out, was 37.5% PS.

It can be seen that very good agreement exists between theory and experiment in most cases. Only in the case of a toluene solution of the copolymer is the difference outside experimental error. This difference corresponds to 2.4% of the spread between the two homopolymer results. Although this sort of error is not at all uncommon in measured composition using dual detector GPC, the good agreement obtained in the other solvents suggests that an incorrect estimate of copolymer composition is not the cause.

This error is not very great, however, and since the project ultimately only uses TTCE as a solvent, it is not considered very important.

4.1.4. Variation of Refractive Index Increments with Molecular Weight

The refractive index increments of a series of PDMS samples in TTCE have been determined. Figure 4.1.1 shows these values plotted against weight average molecular weight, as calculated using GPC/LALLS. Strictly speaking, it would be more correct to plot
against number average molecular weight \(^{91}\), but since only an
indication of the influence of molecular weight is required, this is
not considered important.

Figure 4.1.1 shows that, in going from a molecular weight
of 100,000 to a molecular weight of 10,000, the refractive index
increment increases in a negative direction by less than 2\%. All
samples in this study fall well within the molecular weight range
(except for some of those used for GPC/LALLS column calibrations,
which only fall just outside it). It therefore appears that molecular
weight is not likely to have a significant effect on the results.

It is worth noting that the trend shown here is the opposite
of that observed in toluene by the instrument manufacturers \(^{92}\).

4.1.5. Conclusions

1. In TTCE, equation 2.2.9 appears to be closely
followed for PS/PDMS blends and copolymers. For GPC/LALLS calculations, therefore, the
homopolymer values shown in Table 4.1.1 were
used in conjunction with this equation.

2. There may be a slight deviation from equation
2.2.9 for copolymer solutions in toluene. This
is unimportant for the ultimate GPC/LALLS
analysis, but may make a slight difference to
the copolymer static LALLS calculations.

3. There is a slight variation in refractive index
increment with molecular weight in the range
considered. It is not felt to be significant,
and has been ignored in all further calculations.
Figure 4.1.1. Variation of PDMS refractive index increments $\nu$ (in $\text{cm}^3\text{g}^{-1}$) at $23^\circ\text{C}$ with weight average molecular weights.
<table>
<thead>
<tr>
<th>Solvent</th>
<th>( \text{Sample Measured} )</th>
<th>( \nu (\text{cm}^3 \text{g}^{-1}) )</th>
<th>( \text{Sample Measured} )</th>
<th>( \nu (\text{cm}^3 \text{g}^{-1}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Toluene</td>
<td>APS11T</td>
<td>0.1054</td>
<td>PD18</td>
<td>-0.0892</td>
</tr>
<tr>
<td>THF</td>
<td>APS11T</td>
<td>0.1888</td>
<td>PD17</td>
<td>0.0033</td>
</tr>
<tr>
<td>TTCE</td>
<td>APS11T</td>
<td>0.0934</td>
<td>PD18</td>
<td>-0.0932</td>
</tr>
</tbody>
</table>

Table 4.1.1: Refractive index increment results \( \nu \) for PS and PDMS in various solvents at 23°C.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>( \text{PS/PDMS Blend Measured} )</th>
<th>( \text{PS/PDMS Blend Theory} )</th>
<th>( \text{B21 Copolymer Measured} )</th>
<th>( \text{B21 Copolymer Theory} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Toluene</td>
<td>-0.0187</td>
<td>-0.0163</td>
<td>-0.0256</td>
<td>-0.0302</td>
</tr>
<tr>
<td>THF</td>
<td>0.0681</td>
<td>0.0682</td>
<td>0.0620</td>
<td>0.0616</td>
</tr>
<tr>
<td>TTCE</td>
<td>-0.0250</td>
<td>-0.0249</td>
<td>-0.0368</td>
<td>-0.0367</td>
</tr>
</tbody>
</table>

Table 4.1.2: Refractive index increment results (in \( \text{cm}^3 \text{g}^{-1} \)) for a blend and a copolymer of PS and PDMS at 23°C, and their theoretical values.
Section 4.2

"Static" Low Angle Laser Light Scattering Results

4.2.1. Aims of Section

1. To check that homopolymer molecular weights as calculated using LALLS are independent of the solvent used in their determination.

2. To compare blend molecular weight and heterogeneity parameters with those calculated theoretically to assess the accuracy of copolymer light scattering calculations.

3. To establish molecular weight and heterogeneity parameters for a copolymer, for comparison with those obtained using GPC/LALLS.

4.2.2. Homopolymer Results

The measured homopolymer molecular weights are shown in Table 4.2.1, together with the error obtained from the least squares analysis used in their calculation. This is an estimate of the intercept error, corresponding to a coefficient of variation rather than a maximum error value. Errors of around 2% are also possible due to incorrect refractive index increments.

Experimental error can therefore be seen to be sufficient to account for any variation in measured molecular weight values observed on changing solvent.

4.2.3. Blend and Copolymer Results

The measured apparent molecular weight values for a blend (the homopolymer mixture used in Subsection 4.1.3) and B21 copolymer
are shown in Table 4.2.2. The errors quoted are those calculated from the linear regression analysis, as described in Subsection 4.2.2.

It can be seen that the variations in the measured apparent molecular weights between solvents are greater than can be accounted for from experimental error. It is therefore reasonable to use these values to calculate heterogeneity parameters P, Q, and H. The calculated heterogeneity parameters, together with the values obtained for the weight average molecular weights of the two components and the overall sample, are shown in Table 4.2.3. The value of $Q_{\text{max}}$ used to calculate $H$ is calculated according to equation 2.2.19. In the case of the blend, theoretical values obtained from the homopolymer molecular weights are also shown.

On comparing measured blend values with those calculated theoretically, it can be seen that only the values of $Q$, $H$, and $\overline{M}_w$ are close to their theoretical values. Figure 4.2.1 shows the experimental and theoretical curves, corresponding to equation 2.2.12, used in deriving these values. As the various molecular weights are obtained from values near the bottom of the curve (see Figure 2.2.1) it is easy to see how large errors can occur in their evaluation. This is also true of the heterogeneity parameter $P$. The overall shape of the curve, and hence the value of $Q$, is very close to that expected theoretically. The close agreement found for $\overline{M}_w$ is because one of the solvents used was THF, which is almost isoreflective with PDMS, so that the PS component was effectively looked at in isolation.

It is worth noting that, although this analysis gives a satisfactory $Q$ value, the error in the results is greater than expected. Although a large error in the overall refractive index increment and hence $(v_A - v_B)/v$, is likely, this cannot be considered independently of the $M^*$ value. For this reason error bars corresponding
to errors in $v$ are not horizontal. Figure 4.2.1 shows error bars corresponding to an error of $\pm 0.001 \text{ cm}^3 \text{ g}^{-1}$ in $v$. They do not have a large effect on the overall curve. The remaining discrepancy is larger than the error observed in Subsection 4.2.2 for homopolymers. This appears to be in contradiction with the fact that least squares calculations for the blend generally give a smaller error than for the homopolymers in the calculation of molecular weights.

In the case of a copolymer, having less compositional heterogeneity, the calculated molecular weight values should be more accurate and the heterogeneity parameters less accurate than for a blend.

4.2.4. Conclusions

1. Within experimental error, homopolymer molecular weights obtained using LALLS are independent of the solvent used in their determination.

2. A value of the compositional heterogeneity parameter $Q$ which is in good agreement with the theoretical value can be obtained for samples of high compositional heterogeneity.

3. A large error is likely in calculated molecular weight values for samples of high compositional heterogeneity, unless solvent refractive indices are carefully selected.

4. An individual blend component molecular weight can be accurately determined by choosing a solvent isorefractive with the other component, and this should be expected to hold true for copolymers also.
5. There is a slight disagreement between theory and experiment in the case of blend results. If this is due to experimental error, it is greater than that observed for homopolymer LALLS results.
Figure 4.2.1. The apparent molecular weight $M^*$ of a PS/PDMS blend plotted against $(\gamma_{PS} - \gamma_{PDMS})/\gamma$, where the $\gamma$ values represent the appropriate refractive index increments. The solid line represents the experimental curve, and the dashed line the theoretical one. Error bars are shown corresponding to errors in $\gamma$ only.
Table 4.2.1: Homopolymer molecular weights and estimated errors obtained using LALLS in different solvent at 23°C.
<table>
<thead>
<tr>
<th>Sample</th>
<th>Toluene</th>
<th>THF</th>
<th>TTCE</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>M*</td>
<td>Error</td>
<td>M*</td>
</tr>
<tr>
<td>Blend</td>
<td>1,840,000</td>
<td>0.40%</td>
<td>188,000</td>
</tr>
<tr>
<td>B21 Copolymer</td>
<td>125,000</td>
<td>0.85%</td>
<td>54,800</td>
</tr>
</tbody>
</table>

Table 4.2.2: Blend and copolymer apparent molecular weights and their estimated errors using LALLS in different solvents at 23°C.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Blend</th>
<th>B21 Copolymer</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Measured</td>
<td>Theory</td>
</tr>
<tr>
<td>P</td>
<td>13,700</td>
<td>8,600</td>
</tr>
<tr>
<td>Q</td>
<td>14,000</td>
<td>14,400</td>
</tr>
<tr>
<td>( \bar{M}_w )</td>
<td>28,300</td>
<td>52,300</td>
</tr>
<tr>
<td>( \bar{M}_{PS} )</td>
<td>75,300</td>
<td>75,400</td>
</tr>
<tr>
<td>( \bar{M}_{PDMS} )</td>
<td>12,800</td>
<td>38,500</td>
</tr>
<tr>
<td>H</td>
<td>1.15</td>
<td>1.00</td>
</tr>
</tbody>
</table>

Table 4.2.3: Blend and copolymer heterogeneity parameters and molecular weight values obtained using LALLS.
Section 4.3

Dual Concentration Detector Gel Permeation Chromatography

4.3.1. Aims of Section

1. To make use of GPC runs and viscometry to check that TTCE is a suitable GPC solvent for the samples investigated.

2. To investigate the validity of dual concentration detector GPC in determining compositions.

3. To investigate the validity of dual concentration detector GPC in obtaining MWD's.

4.3.2. Viscometry Results

Viscometry measurements were made on PS and PDMS homopolymers in TTCE and chloroform at 25°C. Using published Mark-Houwink parameters for the chloroform solutions of PS and PDMS, the viscosity average molecular weight value (i.e., the value obtained using equation 2.3.3) for each sample was obtained, as shown in Table 4.3.1. These values were then applied to the TTCE solution results to yield Mark-Houwink exponents of 0.75 for PS and 0.84 for PDMS. Such an analysis is by no means rigorous, but only approximate values, for comparative purposes, were required for this part of the experimental programme.

The Mark-Houwink exponent $a$ gives an indication of the solubility of a polymer type in a particular solvent. A higher $a$ value indicates greater solubility, values greater than 0.8 being seldom encountered. The lower limit of $a$ is 0.5. The values obtained here are consistent with TTCE being a good solvent for both homopolymers (and hence both copolymer components), i.e., they both interact strongly with the solvent. This suggests that the
GPC should proceed in a straightforward manner through size exclusion processes.

4.3.3. Column Calibration

The GPC columns were calibrated using narrow MWD PS standards. All peak times, measured on the RI detector trace, were corrected to a flow rate of 1 cm$^3$ min$^{-1}$ (see Subsection 3.4.3). A best fit manual plot of the results is shown in Figure 4.3.1.

For all GPC results presented in this Section, molecular weights were calculated using universal calibration procedures represented by equation 2.3.5. The Mark-Houwink parameters used in their calculation are those shown in Table 4.3.2. The values have no relevance to the arguments used in this Section, so these values have been chosen to be consistent with the work presented in Section 4.4, their evaluation being described in that Section.

4.3.4. Homopolymer GPC Runs

As no appreciable PS signal was observed on the IR detector set at 9.45 μm, a comparison of homopolymer IR and RI traces was only realistically possible using PDMS samples. A series of such samples was run, and results from the two detector traces compared in each case. The delay between the two detector traces was measured directly from the marker peak positions.

A comparison of the molecular weight averages obtained using each detector is shown in Table 4.3.3. Note the inclusion of the average molecular weight, $M_z$, in these results. This quantity is defined as:

$$\bar{M}_z = \frac{\sum N_i M_i^3}{\sum N_i M_i^2}$$  \hspace{1cm} (4.3.1)

The $\bar{M}_z$ values are in good agreement in each case, the worst agreement being obtained for the $\bar{M}_n$ values. Since the $\bar{M}_z$
value is always dominated by the higher molecular weight species in the averaging process, this implies agreement at the high molecular weight end of the chromatograms but not at the low end. A typical comparison of the two traces, drawn with their marker peaks aligned, is shown in Figure 4.3.2, which shows the IR trace to have a longer low molecular weight tail. The same effect occurs for both high and low molecular weight samples, so it appears that any disagreement between detectors is not an absolute function of elution volume.

One possible reason for disagreement between detectors is instrumental damping, due to using too large a meter response. A 40s IR meter response was used throughout this study. Table 4.3.4 shows that if a 1s meter response were used instead there would be no change. Unless there is some inherent damping present in the IR instrument (or the chart recorder associated with it) which is unaffected by adjusting the meter response, therefore, instrumental damping is not the reason.

Another possibility would be a change in instrumental response with molecular weight. In the case of the RI detector, it has been shown in Subsection 4.1.4 that this change would be small and would, in any case, have the opposite effect to that observed here. Although such an effect could exist on the IR detector, it seems unlikely that it would be sufficient to display an IR signal while no RI signal was seen (as seen on the low molecular weight tail), and the effect would be expected to drop off significantly for higher molecular weight samples.

A third explanation would be that some sample is withheld in the IR sample cell, either due to cell geometry or because of adsorption onto the cell windows. Of the three reasons mentioned here, this seems the most likely.

The detector inconsistencies mentioned above are liable to cause an error of about 7.5% in measured homopolymer $\bar{M}_w$ values (although this error may be considerably less for narrower MWD
samples). There should also be an effect on calculated blend or copolymer compositions, and this will be examined in Subsection 4.3.6.

4.3.5. **Concentration Detector Calibrations**

GPC runs on several concentrations of PS and PDMS homopolymer solutions have been used to calibrate the concentration detectors. Areas under the chromatogram peaks were calculated and corrected to a flow rate of 1 cm$^3$ min$^{-1}$. The results are shown in Figure 4.3.3, together with the best straight lines obtained using a linear regression analysis.

In all cases there is a good linear relationship between detector response and concentration, although for the PDMS results the plot does not accurately go through the origin. This may be due to some systematic error in interpretation (e.g. in drawing in the baseline) or in the experimental system (e.g. the withholding of sample in the IR cell, as suggested in Subsection 4.3.5).

For all the composition calculations made in this study, the gradients obtained using linear regression have been used in equations 2.5.3 - 2.5.5.

4.3.6. **Blend Results**

Homopolymer blends (mixtures of APS6T and PD16) of PS and PDMS were made up and run on the GPC system. At each elution volume the concentration of each component was calculated using equations 2.5.3 and 2.5.4. The molecular weight of each component was calculated using the column calibration together with the Mark-Houwink parameters shown in Table 4.3.2. Thus it was possible to calculate an MWD for each component as well as the overall blend composition. A typical computer printout is shown in Figure 4.3.4.
The MWD's of the component homopolymers, as calculated from the results of the various blend GPC runs, are shown in Figure 4.3.5, and the overall results summarised in Table 4.3.5.

The PDMS MWD's are in good agreement with the MWD obtained from a GPC RI trace of original homopolymer, regardless of blend composition. In the case of the PS MWD's, however, this is not true of the cases where only a small proportion of PS was present in the blend. A very poor PS MWD is obtained for the 20.5% PS sample, the distribution appearing as two distinct peaks. The PS $M_n$ and the $M_w$ values reflect this. All other $M_w$ values, for both components, are very close to those expected from homopolymer GPC results. The $M_n$ values show less good agreement. It is normal to expect GPC to produce more accurate $M_w$ than $M_n$ values, but the inconsistencies between the two detectors at the low molecular weight end of the MWD are likely to accentuate this trend. This is also believed to be the reason for the distortion of the PS MWD's and for the incorrect calculation of the 20.5% PS sample. The concentration correction, i.e. the ratio of the concentration of polymer injected to that calculated from detector responses, is also worst for one of the 20.5% PS runs. All the other calculated compositions and overall concentrations are in good agreement with theory.

Thus, for this system, the dual concentration detector method appears to work well so long as the proportion of PS is not too low. It would appear usable down to about 30% PS, although results at this lower limit should be treated with suspicion. Presumably there is also an upper limit, but it does not appear to have been approached with these samples.

4.3.7. Copolymer Results

A series of PS/PDMS block copolymers were run on the dual concentration detector GPC system. The method of calculation is
described in Section 2.5, the molecular weight at each elution volume being calculated according to equation 2.5.6. A typical computer output is shown in Figure 4.3.6. The calculated copolymer MWD's and the variation of composition with molecular weight are shown in Figure 4.3.7, the overall results being summarised in Table 4.3.6. (Note that all the results presented here are calculated in exactly the same way as they are in the GPC/LALLS copolymer analysis.) For comparison the earlier results obtained using a single IR concentration detector, but running twice at two different wavelengths, are also shown. The results attributed to Taylor show the GPC $M_n$ values obtained for PS blocks, isolated before any addition of PDMS was performed, the copolymer compositions obtained using silicon analysis, and the copolymer $M_n$ value derived using equation 2.6.16. The $M_w$ results attributed to Taylor are derived from his calculated $M_n$ values and the $M_w/M_n$ results he obtained from GPC runs in THF.

Overall composition results are in good agreement, not only with those obtained on the earlier GPC set up, but also with those obtained by Taylor. The worst agreement is for B21. This has the lowest proportion of PS (~30%) so poorer results might be anticipated, judging by the blend results in Subsection 4.3.6.

Overall copolymer $M_w$ results are in good agreement with those obtained earlier using two runs at different IR wavelengths. This is not so true of the various $M_n$ values obtained. The main reason for this is likely to be the necessity of ignoring the extreme low molecular weight end of chromatograms when using the earlier method, due to the presence of spurious peaks (see Section 3.4.2). There are also considerable problems at the low molecular weight end using the RI/IR detector combination, as seen from the blend analysis results, so no great accuracy is expected for the $M_n$ results.

Comparison of the molecular weight results with those obtained by Taylor is very revealing. Taylor's $M_n$ results, obtained directly from the PS homopolymer blocks used in copolymer
synthesis, should give the same $M_n^\text{PS}$ values as obtained after copolymer synthesis provided no PDMS homopolymer is present in the copolymer sample. This is because the number averaging process takes place over all the molecules present, whether or not they contain any PS. Taylor's copolymer $M_n$ values are calculated from the $M_n^\text{PS}$ results, so that the presence of PDMS homopolymer will equally affect these values. $M_w/M_n$ values are subject to the further inaccuracy that only a single GPC detector was used in their determination (detecting only the PS component), so that it had to be assumed that composition did not vary with elution volume (i.e. $P = 0$). This would have an additional effect on his $M_w$ values, but, according to Figure 4.3.7, the main effect would be on samples B12 and B13.

The large disagreement between the molecular weight results observed here and those found by Taylor for samples B12, B13 and B21 suggest that PDMS homopolymer was present in these samples. In the case of B12 and B13 both the shape of the MWD and the large variation of composition with molecular weight suggest something more like a blend. There is nothing to directly suggest this from the B21 traces, however. In the case of the other copolymers, particularly good agreement is generally seen for the copolymer $M_w$ values. Since Taylor's $M_w$ results were derived from $M_n$ values, this suggests that his $M_n$ values were also good, i.e. more accurate than those obtained in this work.

The provisional indications suggested here, i.e. that B16, B20 and B22 are pure copolymers but B12, B13 and possibly B21 are more like blends, will be useful for comparison with the GPC/LALLS heterogeneity results looked at in Subsection 4.4.4.

4.3.8. **Conclusions**

1. TTCE is a good solvent for both copolymer components.
2. There is a discrepancy between RI and IR traces at the low molecular weight end of the chromatograms, but good agreement at the high molecular weight end. The discrepancy may be due to the withholding of sample in the IR cell.

3. Detector responses vary linearly with concentration. There may be a slight zero offset, however, due to interpretation errors or artefacts from the instrumentation.

4. Dual concentration detector GPC works well on PS/PDMS samples using the RI/IR detection system so long as sufficient PS is present. Compositions down to 30% PS are considered usable, but results at this lower limit must be treated with suspicion. In general, $\overline{M_w}$ and overall composition results are much more accurate than $\overline{M_n}$ results.

5. It appears very likely that "copolymers" B12 and B13 are close approximations to blends. There is also some question in the case of B21.
Figure 4.3.1. The GPC column calibration of molecular weight against elution volume (in cm$^3$) using narrow MWD PS standards.

Solvent: TTCE

Flow rate: 1 cm$^3$ min$^{-1}$

Column temperature: 80$^\circ$C
Figure 4.3.2. A comparison of the GPC traces obtained from the two concentration detectors for a PDMS sample. The RI trace has been inverted. The dashed lines represent the baselines used in the analysis.

Sample: PD16
Solvent: TTCE
Flow rate: 1 cm³ min⁻¹
Column temperature: 80°C
Figure 4.3.3. Variation of GPC detector responses (in arbitrary units of area under chromatogram peaks) with concentration (in g cm\(^{-3}\)).
Figure 4.3.4. A typical computer output for a blend characterised using dual concentration detector GPC.
Figure 4. 3. 5. MWD’s of blend components as calculated using dual concentration detector GPC.
A typical computer output for a copolymer characterised using dual concentration detector GPC. Note that the quoted component molecular weight values at each elution volume are number average values. Similarly, although component overall $M_w$ and $M_z$ values are quoted, these are only applicable if compositional homogeneity exists at each elution volume.
Figure 4.3.7. Copolymer MWD's (----) and variation of composition with molecular weight (-----) as calculated from dual concentration detector GPC.
<table>
<thead>
<tr>
<th>Sample</th>
<th>Polymer Type</th>
<th>([\eta]_{TTCE})</th>
<th>([\eta]_{CHCl_3})</th>
<th>(\overline{M}_v)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PS2</td>
<td>PS</td>
<td>82.0</td>
<td>108.0</td>
<td>295,000</td>
</tr>
<tr>
<td>APS6T</td>
<td>PS</td>
<td>22.16</td>
<td>26.80</td>
<td>51,000</td>
</tr>
<tr>
<td>PD20</td>
<td>PDMS</td>
<td>37.10</td>
<td>44.65</td>
<td>122,000</td>
</tr>
<tr>
<td>PD15</td>
<td>PDMS</td>
<td>16.13</td>
<td>20.75</td>
<td>45,200</td>
</tr>
</tbody>
</table>

Table 4.3.1: Intrinsic viscosities (in cm\(^3\) g\(^{-1}\)) obtained in chloroform and TTCE at 25°C and viscosity average molecular weights (\(\overline{M}_v\)) obtained from the chloroform results.

<table>
<thead>
<tr>
<th>Polymer Type</th>
<th>(K \times 10^3)</th>
<th>(a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Column calibration standards</td>
<td>6.5</td>
<td>0.75</td>
</tr>
<tr>
<td>PS</td>
<td>6.4</td>
<td>0.75</td>
</tr>
<tr>
<td>PDMS</td>
<td>2.9</td>
<td>0.84</td>
</tr>
</tbody>
</table>

Table 4.3.2: Mark-Houwink \(K\) (in cm\(^3\) g\(^{-1}\)) and \(a\) values used for GPC work.
<table>
<thead>
<tr>
<th>Sample</th>
<th>RI Detector</th>
<th>IR Detector</th>
<th>Ratio of Results</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\overline{M}_n$</td>
<td>$\overline{M}_w$</td>
<td>$\overline{M}_z$</td>
</tr>
<tr>
<td>PD16</td>
<td>17,100</td>
<td>34,900</td>
<td>54,100</td>
</tr>
<tr>
<td>PD16</td>
<td>16,600</td>
<td>35,100</td>
<td>57,300</td>
</tr>
<tr>
<td>PD18</td>
<td>25,500</td>
<td>73,500</td>
<td>124,500</td>
</tr>
<tr>
<td>PD 23</td>
<td>40,900</td>
<td>143,700</td>
<td>239,900</td>
</tr>
</tbody>
</table>

Table 4.3.3: A comparison of the PDMS homopolymer molecular weights obtained using each of the GPC concentration detectors.
Table 4.3.4: The effect of IR instrumental damping on GPC results for PDMS sample PD16.
<table>
<thead>
<tr>
<th>% PS Weighed Out</th>
<th>% PS From GPC</th>
<th>PS $M_n$</th>
<th>PS $M_w$</th>
<th>PDMS $M_n$</th>
<th>PDMS $M_w$</th>
<th>Concentration Correction</th>
</tr>
</thead>
<tbody>
<tr>
<td>20.5</td>
<td>15.8</td>
<td>5,700</td>
<td>30,100</td>
<td>13,800</td>
<td>34,200</td>
<td>0.87</td>
</tr>
<tr>
<td>20.5</td>
<td>16.8</td>
<td>5,300</td>
<td>30,800</td>
<td>12,700</td>
<td>34,400</td>
<td>0.97</td>
</tr>
<tr>
<td>40.2</td>
<td>40.3</td>
<td>8,200</td>
<td>42,700</td>
<td>12,700</td>
<td>34,400</td>
<td>0.95</td>
</tr>
<tr>
<td>40.2</td>
<td>39.6</td>
<td>9,100</td>
<td>44,600</td>
<td>13,800</td>
<td>35,100</td>
<td>0.94</td>
</tr>
<tr>
<td>59.5</td>
<td>61.5</td>
<td>11,100</td>
<td>43,000</td>
<td>12,700</td>
<td>34,600</td>
<td>0.96</td>
</tr>
<tr>
<td>75.9</td>
<td>75.5</td>
<td>9,600</td>
<td>43,900</td>
<td>14,700</td>
<td>35,500</td>
<td>0.95</td>
</tr>
<tr>
<td>Homopolymer</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Results</td>
<td></td>
<td>11,400</td>
<td>43,600</td>
<td>17,100</td>
<td>35,800</td>
<td></td>
</tr>
</tbody>
</table>

Table 4.3.5: Results from dual concentration detector GPC on a series of blends.
<table>
<thead>
<tr>
<th>Copolymer</th>
<th>$\bar{M}_n$</th>
<th>$\bar{M}_w$</th>
<th>Composition (% PS)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>PS</td>
<td>PDMS</td>
<td></td>
</tr>
<tr>
<td></td>
<td>RI/IR GPC</td>
<td>IR/IR GPC</td>
<td>Taylor</td>
</tr>
<tr>
<td></td>
<td>RI/IR GPC</td>
<td>IR/IR GPC</td>
<td>Taylor</td>
</tr>
<tr>
<td></td>
<td>RI/IR GPC</td>
<td>IR/IR GPC</td>
<td>Taylor</td>
</tr>
<tr>
<td></td>
<td>RI/IR GPC</td>
<td>IR/IR GPC</td>
<td>Taylor</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>B12</td>
<td>8,300</td>
<td>13,400</td>
<td>13,600</td>
</tr>
<tr>
<td>B13</td>
<td>4,700</td>
<td>8,800</td>
<td>5,900</td>
</tr>
<tr>
<td>B13</td>
<td>4,600</td>
<td>8,800</td>
<td>5,900</td>
</tr>
<tr>
<td>B16</td>
<td>34,300</td>
<td>39,700</td>
<td>11,700</td>
</tr>
<tr>
<td>B16</td>
<td>39,700</td>
<td>39,700</td>
<td>13,400</td>
</tr>
<tr>
<td>B20</td>
<td>10,700</td>
<td>12,700</td>
<td>2,700</td>
</tr>
<tr>
<td>B20</td>
<td>12,700</td>
<td>12,700</td>
<td>3,200</td>
</tr>
<tr>
<td>B21</td>
<td>3,600</td>
<td>7,700</td>
<td>7,500</td>
</tr>
<tr>
<td>B21</td>
<td>3,700</td>
<td>7,700</td>
<td>7,600</td>
</tr>
<tr>
<td>B22</td>
<td>26,900</td>
<td>30,500</td>
<td>11,300</td>
</tr>
<tr>
<td>B22</td>
<td>27,300</td>
<td>39,500</td>
<td>11,900</td>
</tr>
</tbody>
</table>

Table 4.3.6: Overall results obtained for copolymers using dual concentration detector (RI/IR) GPC. Results obtained using an IR/IR detector system (two runs at two different wavelengths) together with the results obtained by Taylor are also shown for comparison.
Section 4.4

Low-Angle Laser Light Scattering Used With Gel Permeation Chromatography

4.4.1. Aims of Section

1. To establish column calibrations, for both PS and PDMS, from GPC/LALLS results.

2. To use blends to establish the validity of the various heterogeneity and molecular weight values obtained using a GPC/LALLS copolymer analysis.

3. To use GPC/LALLS to characterise copolymers and assess the quality of the results obtained.

4.4.2. Column Calibrations

GPC/LALLS runs were performed on a series of PS and PDMS samples. For each sample, a method developed for use in this study, described in Subsection 2.4.2, was used to calculate an $M_w$ value together with its corresponding elution volume (corrected to $1 \text{ cm}^3 \text{ min}^{-1}$). The resulting values are shown in Figure 4.4.1.

It is convenient to use the column calibration obtained using narrow MWD standards as the basis for the GPC/LALLS calibrations, using the results of the GPC/LALLS runs to "correct" the original calibration curve. A useful way of doing this is to express such a correction in terms of applying a "universal calibration" procedure as described by equation 2.3.5. Thus, suitable Mark-Houwink parameters (whether or not they are "true" Mark-Houwink parameters) can be found to produce corrections consistent with the GPC/LALLS results. In this case, unfortunately, insufficient data was obtained to give an accurate correction to the curve slope.
corresponding to the Mark-Houwink exponent $a$, although run replication may have provided sufficient information. The actual $a$ values obtained using viscometry were therefore used. The Mark-Houwink $K$ value was obtained from the average offset of the GPC/LALLS calibration points (ignoring one obviously spurious PDMS point) from the slope-corrected calibration. The resultant parameters obtained are those shown in Table 4.3.2.

4.4.3. Blend Results

The GPC/LALLS copolymer characterisation method devised for this project (and described in Section 2.6) is intended to be applicable to copolymers of both low and high compositional heterogeneity. It should therefore regard a blend as a copolymer having the maximum possible heterogeneity, thus identifying it as a blend. It should also provide molecular weight values for the components. GPC/LALLS runs have therefore been performed on a series of blends and a heterogeneity value $H_1$ calculated at each elution volume using the method described in Subsection 2.6.3. Each such value should, in the case of a blend, be equal to unity. The values obtained experimentally are plotted against the calculated "copolymer" molecular weights in Figure 4.4.2. A typical computer printout is shown in Figure 4.4.3.

Before looking at the experimental errors in $H_1$, it is worth looking at the errors expected due to the assumptions made in their calculation. One such assumption was that, because only a narrow molecular weight fraction was present at each elution volume, the value of $P_1$ at each elution volume could be taken as zero. The effect of this assumption on the calculated $H_1$ of some typical eluting fractions is shown in Table 4.4.1. In the molecular weight range considered the effect should be fairly small and, in the main, considerably less than the errors seen on the traces in Figure 4.4.2. A second assumption was that the "copolymer" molecular weight
M\text{t}, then treated as the weight average molecular weigh \( \overline{M}_{wi} \), at the \( i \)th elution volume could be calculated according to equation 2.5.6:

\[
\log M_i = W_i \log M_A i + (1-W_i) \log M_B i
\]

In fact, the true weight average value would be:

\[
\overline{M}_{wi} = W_i M_A i + (1-W_i) M_B i
\]

(4.4.1)

The effect of using equation 2.5.6 rather than equation 4.4.1 is shown in Table 4.4.2, and the errors produced can be seen to be negligible. It appears, therefore, that the main errors in the calculated \( H_i \) values are experimental rather than due to any fundamental oversimplifications in the analysis.

It is to be expected that the accuracy of the calculated \( H_i \) values should be directly related to both the size of the concentration detector signals (effectively corresponding to the "copolymer" MWD heights) and that of the LALLS signal. Because LALLS is most sensitive towards the high molecular weight end of the chromatogram (see Figure 4.4.4), therefore, it is this end of the MWD which should give the most accurate \( H_i \) values. This is, in general, what is observed in Figure 4.4.2. Only in the case of the blend containing 75.9% PS is this not so.

Another factor in determining the accuracy of the calculated \( H_i \) values is the overall composition at each elution volume. The largest deviation in calculated \( H_i \) generally occurs at the extremes of calculated composition. This most obviously occurs in the sample containing 20.5% PS. As its calculated composition approaches 100% PS (although this is obviously not the true value - see the PS MWD calculated for this blend shown in Figure 4.3.5), the calculated \( H_i \) value becomes ridiculously large. There are two reasons why this should be so. Firstly, a small error in the measured composition will result in a large error in \( Q_{i,\text{max}} \):

\[
(= W_i (1-W_i) [((1-W_i)M_A i + W_i M_B i])],
\]

and hence \( H_i \), when either \( W_i \)
or \((1 - W_i)\) is small. It was shown in Subsection 4.3.6 that at low PS percentages the calculated composition was particularly poor, so it is not surprising that in the case of the 20.5\% PS sample such a deviation should be seen. Secondly, the apparent LALLS molecular weight tends to increase as the absolute value of the copolymer refractive index increment \(v\) decreases, thus increasing the accuracy of \(H_i\). In this case, the \(v = 0\) condition is satisfied at 49.9\% PS, so, in this respect, this is where the most accurate \(H_i\) values should be obtained. (At this composition the assumptions leading to the errors shown in Tables 4.4.2 and 4.4.3 should also become completely valid.) Both the above reasons are expected to contribute to the fact that the 40.2\% PS and 59.5\% PS samples give the best values for \(H_i\).

A possibly more physically meaningful way of looking at the data is shown in Figures 4.4.5 - 4.4.8. At each elution volume, the GPC/LALLS copolymer analysis is capable of producing both an \(\bar{M}_{wi}\) and an \(\bar{M}_{ni}\) value for each component (equations 2.6.12, 2.6.13, 2.6.17, and 2.6.18). In the case of a copolymer which is compositionally homogeneous at each elution volume the component \(\bar{M}_{wi}\)'s are given by:

\[
\bar{M}_{wi} = \bar{M}_{ni} A
\]  
(4.4.2)

\[
\bar{M}_{wi} = \bar{M}_{ni} B
\]  
(4.4.3)

where

\[
\bar{M}_{ni} A = W_i M_i
\]  
(2.6.16)

\[
\bar{M}_{ni} B = (1 - W_i) M_i
\]  
(2.6.17)

In the case of a blend, however, the molecular weight of each component should be equal to the "copolymer" molecular weight \(M_i\) at each elution volume (the analysis considers all species at a particular elution volume as having the same molecular weight). The component \(\bar{M}_{wi}\) values should be a measure of the actual component molecular weight at elution volume \(i\). Therefore, for a blend:
In theory, both component $\bar{M}_{wi}$'s of a blend should fall on plots represented by equations 4.4.4 and 4.4.5. Their actual positions, compared with the theoretical plots, are shown in Figures 4.4.5 - 4.4.8, together with the corresponding $\bar{M}_{ni}$ values for each component, determined according to equations 2.6.16 and 2.6.17. The same features as observed in Figure 4.4.2 are to be seen here, but some of the excesses are less obvious. Nearly all $\bar{M}_{wi}$ PS and $\bar{M}_{wi}$ PDMS points fall very much closer to the $\bar{M}_i$ values than to the $\bar{M}_{ni}$ PS and $\bar{M}_{ni}$ PDMS curves respectively, i.e. the behaviour expected of a blend is fairly well followed.

Table 4.4.3 shows the overall molecular weight and heterogeneity parameters calculated for these samples. Note that the component $\bar{M}_n$'s are not expected to be the same as for the original component homopolymers. This is because the number averaging process takes place over both types of homopolymer molecule present. Errors in calculated molecular weights are about the same as those observed using a straightforward dual concentration detector GPC blend analysis (see Table 4.3.5). The only exception to this is that the 75.9% PS sample the $\bar{M}_w$ PDMS value is significantly overestimated. One can see from Figure 4.4.8 how the $\bar{M}_w$ PDMS values are consistently overestimated for this blend, especially where there is a very low PDMS content. As well as errors due to overestimating the compositional heterogeneity there is the problem of assuming that both components at each elution volume have the same molecular weight. This is bound to have a bad effect on the molecular weight calculations for the minority component of a blend. However, in this case, where both component column calibrations are very similar (see Figure 4.4.1) this should not be a significant problem.

Table 4.4.3 shows the $P$ values obtained to be generally about 500 too low. This will be partly due to ignoring $P_1$ at each elution volume. The 20.5% PS sample, however, shows much
worse agreement, actually giving the wrong sign for $P$. Since $P$ is a measure of the variation of composition with molecular weight, and it has already been established that the curve representing this for the 20.5% PS sample has been considerably distorted, a large error in $P$ is to be expected in this case for experimental reasons.

The errors in $Q$ are greatest at the extremes of composition, as with the $H_1$ values. These errors can be divided into random errors (mainly due to poor LALLS baselines) and systematic errors. In this sense, systematic means systematic over all runs for a particular sample, not over all possible PS/PDMS samples. Thus the inconsistencies between the two concentration detectors and the effect of ignoring $P_i$ at each elution volume are likely to be important contributors to such an error. A more detailed discussion of the errors in $Q$ and $H$ will be made in Subsection 4.4.4.

The overall heterogeneity parameter $H$ is in much better agreement with theory (unity) than either $Q$ or the individual $H_1$ values (see Figure 4.4.2). An average error of 0.04 is achieved.

In all cases, the parameters obtained are in better agreement with theory than those obtained using static LALLS in Subsection 4.2.3, with the exception of $Q$ and $M_w^{PS}$ (see Table 4.2.3). However, this is an unfair comparison because more suitable solvents could have been chosen for measuring particular parameters with static LALLS (using mixed solvents if necessary).

4.4.4 Copolymer Results

The PS/PDMS copolymer samples have been run on the GPC/LALLS system and analysed using exactly the same method as used in Subsection 4.4.3. The variation of the heterogeneity parameter $H_1$ with copolymer molecular weight $M_1$ is shown in Figure 4.4.9.

In theory:

$$0 < H_1 < 1$$

(4.4.6)
H_i = 0 corresponding to a homogeneous copolymer and H_i = 1 corresponding to a blend. Similarly:

\[ \frac{M_{ni}}{N_i} \frac{PS}{PS} < \frac{M_{wi}}{N_i} \frac{PS}{PS} < \frac{M_i}{N_i} \]  (4.4.7)

\[ \frac{M_{ni}}{N_i} \frac{PDMS}{PDMS} < \frac{M_{wi}}{N_i} \frac{PDMS}{PDMS} < \frac{M_i}{N_i} \]  (4.4.8)

These, looked at in this way, \( \frac{M_{wi}}{N_i} \frac{PS}{PS} = \frac{M_{ni}}{N_i} \frac{PS}{PS} \) and \( \frac{M_{wi}}{N_i} \frac{PDMS}{PDMS} = \frac{M_{ni}}{N_i} \frac{PDMS}{PDMS} \) correspond to a homogeneous copolymer, and \( \frac{M_{wi}}{N_i} \frac{PS}{PS} = \frac{M_{wi}}{N_i} \frac{PDMS}{PDMS} \) corresponds to a blend. Although the \( H_i \) values given in Figure 4.4.9 give an instantaneous indication of copolymer heterogeneity, it may be more physically meaningful to look at the data as presented in Figures 4.4.10 - 4.4.15. The interpretation of the data in either form gives the following results:

1. B13 is a homopolymer blend of high molecular weight PS with low molecular weight PDMS.

2. B12 is a homopolymer blend of high molecular weight PS with low molecular weight PDMS. However, there is also some copolymer present, the middle part of the MWD consisting predominantly of copolymer.

3. B21 is a high molecular weight copolymer together with a blend of lower molecular weight homopolymers.

4. B16, B20, and B22 are compositionally more homogeneous and are likely to be pure copolymer.

All this is in agreement with the provisional suggestions given in Subsection 4.3.7, following on from dual concentration detector GPC results. Some idea of the errors involved is needed, however, before drawing any definite conclusions.

A summary of the overall results is given in Table 4.4.4.
As most of the samples have been run in duplicate it is possible to make an estimate of the random errors involved. The error in \( Q \) is more consistent than the error in \( H \), as can be seen from Table 4.4.4. This is to be expected because \( Q \) is proportional to molecular weight (as is the LALLS signal largely dominating the random error), whereas \( H \) is not. Thus the absolute error in \( Q \) is independent of molecular weight, but the relative error in \( Q \) (as reflected in \( H \)) increases markedly with decreasing molecular weight. The random error in \( Q \) should also be affected by composition, but this is not noticeable in these results. The mean standard deviation of the results for \( Q \) is 210, and it seems reasonable that this value should also approximately hold true for the blend results. Assuming random errors in \( H \) are totally reflected as random errors of 210 in \( Q \), an estimate of the random errors in \( H \) for the blend runs described in Subsection 4.4.3 can be obtained, giving the results shown in Table 4.4.5. The remaining errors in \( H \) should be systematic. Both the error due to ignoring \( P_i \) at each elution volume and that due to concentration detector inconsistencies are likely to decrease (in an absolute sense) with decreasing \( H \). The incorrect calculation of \( M_i \) values, however, due to equation 2.5.6 not being followed, is likely to cause errors which will not decrease with decreasing \( H \). It is not likely that such deviations will be large, however, unless the two copolymer blocks are highly incompatible. Thus it seems fairly safe to expect the systematic errors in \( H \) observed for the copolymers not to exceed the systematic errors in \( H \) observed for the blends. The average blend systematic error comes out as 0.02. If a random error of 210 in \( Q \) and a systematic error of 0.02 in \( H \) is assumed for all copolymers, the errors in \( H \) will be those shown in Table 4.4.6.

B20 has a very large error in \( H \) due to its low molecular weight (and the high proportion of PS present). The analysis has been sufficiently sensitive to show the copolymer as fairly homogeneous in composition, but the technique has been used at its
limits. No other samples appear to have unreasonable errors.

B21 results can be compared with those obtained earlier using static LALLS. Such a comparison is shown in Table 4.4.7. There is an approximate agreement between the results, but a greater disagreement than would be expected simply for the GPC/LALLS errors as estimated in Table 4.4.6. For the blends, GPC/LALLS appears to give better results than static LALLS (using the particular solvents mentioned), and it may be expected that this should also hold true for a copolymer such as this. However, for this particular sample the GPC/LALLS results must be treated with caution because B21 is approaching the lower limit of composition (expressed at % PS) at which the dual concentration detector analysis work satisfactorily. A supporting argument for the GPC/LALLS results is the straightforward shape of the composition curve. It is unlikely that GPC/LALLS should give an incorrect analysis at the high molecular weight end of the MWD, but at the low molecular weight end GPC/LALLS may tend to overestimate heterogeneity due to imperfect resolution. This has not been noticed for any of the other samples, however. Also, static LALLS gives a sizeable value to H (even though there is not exact agreement) and comparison of dual detector GPC results with the $M_n$ result of Taylor (see Subsection 4.3.7) suggests the presence of homopolymer. The analysis of B21 as a copolymer at high molecular weight and a blend at low molecular weight therefore fits in well with the other available evidence.

The H value of 1.01 for B13 suggests that it is a pure blend, and the value of 0.82 for B12 suggests it is predominantly blend. The two samples were therefore analysed as blends using the same method as used in Subsection 4.3.6. The MWD's obtained are shown in Figure 4.4.16. The high molecular weight shoulder on the PDMS MWD for B12 suggests that copolymer is present. It is not clear, however, whether the low molecular weight tail on the PS MWD of B13 is due to copolymer or to detector inconsistencies.

Even if B12 and B13 are essentially blends, it is likely that
their PS components are much the same as the original PS blocks intended for their copolymerisation. The $M_n$ value of these blocks has been measured by Taylor, as explained previously. If the samples are true blends (and were when he made his measurements), the $M_w/M_n$ values obtained by Taylor, ostensibly for the whole sample, were in fact those of the PS components because he used a solvent/detector system sensitive only to PS. For a known blend, therefore, both the $M_n$ and the $M_w$ values of the PS component can be obtained from Taylor's data. These values for B12 and B13 are shown in Table 4.4.8, together with the results of dual detector blend analyses described above. Although the PS $M_n$ values are in poor agreement, probably because of detector inconsistencies, the $M_w/PS$ value for B13 is in very good agreement, supporting the view that this sample is a blend. For B12 the agreement is not so good, but this is to be expected because some copolymer is believed to be present in the sample.

B16, B20 and B22 are likely to be pure block copolymers. If so, random coupling statistics may well be followed in their synthesis, leading to equations 2.2.22 and 2.2.23:

$$P = W(1-W) \left[ M_n^{PS} - M_n^{PS} \cdot M_n^{PDMS} - M_n^{PDMS} \right]$$

$$Q = W(1-W) \left[ (1-W)(M_w^{PS} - M_w^{PS}) + W(M_w^{PDMS} - M_w^{PDMS}) \right]$$

The values of $P$ and $Q$ obtained using these equations are given in Table 4.4.9. The first column for each parameter represents the values calculated using only molecular weight results from this analysis. The agreement of these results with those measured is not very good, but of the right order of magnitude, although in the case of B12 and B13, expected to behave like blends rather than block copolymers, the agreement is very close. This apparently illogical result can be explained by the fact that both these samples have very low calculated $M_n$ values which means that equations 2.2.22 and 2.2.23 tend to approach the blend equations (equations
2.2.18 and 2.2.19). The generally poor $M_n$ values produced by this analysis are likely to distort all the calculations using equations 2.2.22 and 2.2.23. These equations have also been evaluated, therefore, using $\bar{M}_n$ values derived from the $\bar{M}_{PS}$ values measured by Taylor and the calculated copolymer composition. These results are shown in the second column for each parameter in Table 4.4.9. Such a calculation is only valid if no PDMS homopolymer exists in the sample, hence the ridiculous results obtained for B12 and B13 (negative $Q$ values are theoretically impossible). However, results for B16 and B22 are in excellent agreement, as are those for the first B20 run. This strongly suggests that good values of $P$ and $Q$ are being produced by this method, and that random coupling statistics are applicable to copolymers B16, B22, and maybe B20. It is surprising, however, that such good agreement should be obtained between independent GPC measurements.

The overall interpretation of the $H_i$ results given at the start of this Subsection appears correct, therefore, together with the additional information that B16 and B22 follow random coupling statistics. This is probably also true of B20, but the error is too great to give a definite answer.

4.4.5. Conclusions

1. To obtain a full GPC/LALLS column calibration without resorting to assumptions requiring Mark-Houwink exponents (and universal calibration procedures) one would need more calibration points than were obtained in this study. The method of using a combination of GPC/LALLS results and known Mark-Houwink exponents gives satisfactory results in this case, but is not ideal.

2. Errors in $H$ are considerably less than
individual $H_i$ errors. For this type of sample the contributions to errors in $H$ can be considered as a random error of about 210 in $Q$ ($\equiv 210 \times H/Q$ in $H$) together with a systematic error of about 0.02 in $H$.

3. It may be convenient to look at individual $\bar{M}_{wi}^A$ and $\bar{M}_{wi}^B$ values to get a physical picture of what is happening in the copolymer.

4. Molecular weights obtained for blend components using GPC/LALLS have errors of about the same size as do those obtained using a dual concentration detector blend analysis.

5. Concentration detector inconsistencies may affect heterogeneity calculations. This has not caused serious problems in the calculation of overall heterogeneity parameters, however. More significant is the error in the various calculated $\bar{M}_n$ values.

6. Although imperfect column resolution may be expected to cause an overestimation of lower molecular weight $H_i$ values, this has not been noticeable in these results (although the accuracy of $H_i$ decreases markedly with decreasing molecular weight due to the low LALLS response).

7. Large errors in heterogeneity results are likely for copolymers having $M_w$ values of less than 25,000 due to the poor LALLS response.

8. Agreement between calculated and theoretical overall heterogeneity parameters is generally good, suggesting that the GPC/LALLS method is working successfully.
Figure 4.4.1. Points obtained for a column calibration using GPC/LALLS, as compared to the original column calibration using narrow MWD PS standards. The elution volume is in units of cm$^3$.

Solvent: TTCE
Flow rate: 1 cm min$^{-1}$
Column temperature: 80°C
Figure 4.4.2. Plots of the calculated compositional heterogeneity $H_1$ (——) of PS/PDMS (8-3.4) blends, together with their theoretical values ($H_1 = 1$) (---), calculated "copolymer" MWD (-----), and the calculated variation of composition with molecular weight (--------).
Figure 4.4.3. A typical GPC/LALLS "copolymer" printout (in this case, the results obtained for a blend).
A comparison of the three detector traces obtained for a typical blend (40.2% PS), including baselines used for the analysis. Note the way in which the low molecular weight end of the IR trace was not used. The spikes on the LALLS trace were due to "dust" particles, and could safely be ignored in the calculation.
Figure 4.4.5. Variation of calculated blend component molecular weights (using GPC/LALLS and treating each blend as an unknown copolymer) with "copolymer" molecular weight $M_1$.

Note that only every fourth point is shown.
Figure 4. Variation of calculated blend component molecular weights (using GPC/LALLS and treating each blend as an unknown copolymer) with "copolymer" molecular weight $M_i$. Note that only every fourth point is shown.
Figure 4.4.7. Variation of calculated blend component molecular weights (using GPC/LALLS and treating each blend as an unknown copolymer) with "copolymer" molecular weight $M_i$. Note that only every fourth point is shown.
Figure 4.4.8. Variation of calculated blend component molecular weights (using GPC/LALLS and treating each blend as an unknown copolymer) with "copolymer" molecular weight $M_i$. Note that only every fourth point is shown.
Figure 4.4.9. Variation of the calculated heterogeneity parameter $H_1$ with molecular weight (---). Also shown on the plots are the maximum theoretical $H_1$ values ($H_1 = 1$) (---), the calculated copolymer MWD (--.--), and the variation of composition with molecular weights (------).
Figure 4.4.10. Variation of calculated copolymer component molecular weights with copolymer molecular weight. Note that only every second point is shown.
Figure 4.4.11. Variation of calculated copolymer component molecular weights with copolymer molecular weight. Note that only every second point is shown.
Figure 4.4.12. Variation of calculated copolymer component molecular weights with copolymer molecular weight. Note that only every second point is shown.
Figure 4.4.13. Variation of calculated copolymer component molecular weights with copolymer molecular weight. Note that only every second point is shown.
Figure 4.4. Variation of calculated copolymer component molecular weights with copolymer molecular weight. Note that only every second point is shown.
Figure 4.4.15. Variation of calculated copolymer component molecular weights with copolymer molecular weight. Note that only every second point is shown.
Figure 4.4.16. "Copolymers" B12 and B13 analysed as blends (--- = PS component, ---- = PDMS component). Note that the MWD's for both components have been separately normalised.
## Component Molecular Weights

<table>
<thead>
<tr>
<th>Component Molecular Weights</th>
<th>Error in $H_i$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>20% PS</td>
</tr>
<tr>
<td>PS</td>
<td>PDMS</td>
</tr>
<tr>
<td>1,000</td>
<td>1,100</td>
</tr>
<tr>
<td>3,000</td>
<td>3,100</td>
</tr>
<tr>
<td>10,000</td>
<td>9,800</td>
</tr>
<tr>
<td>30,000</td>
<td>27,900</td>
</tr>
<tr>
<td>100,000</td>
<td>87,600</td>
</tr>
<tr>
<td>300,000</td>
<td>248,900</td>
</tr>
<tr>
<td>1,000,000</td>
<td>782,300</td>
</tr>
</tbody>
</table>

Table 4.1: Errors in $H_i$ due to assuming $P_i = 0$ for some typical eluting fractions from PS/PDMS blends. A positive sign indicates an increase in the calculated $H_i$ value, and vice versa.
<table>
<thead>
<tr>
<th>Component Molecular Weight</th>
<th>Error in H₁</th>
<th>20% PS</th>
<th>40% PS</th>
<th>60% PS</th>
<th>80% PS</th>
</tr>
</thead>
<tbody>
<tr>
<td>PS . PDMS</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1,000 1,100</td>
<td>0.0004</td>
<td>0.0004</td>
<td>0.0004</td>
<td>0.0004</td>
<td></td>
</tr>
<tr>
<td>3,000 3,100</td>
<td>0.00007</td>
<td>0.00007</td>
<td>0.00007</td>
<td>0.00007</td>
<td></td>
</tr>
<tr>
<td>10,000 9,800</td>
<td>0.00002</td>
<td>0.00002</td>
<td>0.00002</td>
<td>0.00002</td>
<td></td>
</tr>
<tr>
<td>30,000 27,900</td>
<td>0.0002</td>
<td>0.0003</td>
<td>0.0003</td>
<td>0.0003</td>
<td></td>
</tr>
<tr>
<td>100,000 87,600</td>
<td>0.0008</td>
<td>0.0009</td>
<td>0.0009</td>
<td>0.0008</td>
<td></td>
</tr>
<tr>
<td>300,000 248,900</td>
<td>0.001</td>
<td>0.0002</td>
<td>0.0002</td>
<td>0.002</td>
<td></td>
</tr>
<tr>
<td>1,000,000 782,300</td>
<td>0.002</td>
<td>0.0003</td>
<td>0.0003</td>
<td>0.003</td>
<td></td>
</tr>
</tbody>
</table>

Table 4.4.2: Errors in H₁ due to the incorrect calculation of "copolymer" molecular weights at some typical eluting fractions from PS/PDMS blends. In all cases the error would tend to increase the calculated H₁ values.
<table>
<thead>
<tr>
<th>% PS</th>
<th>PS Component</th>
<th>PDMS Component</th>
<th>Overall Sample</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\bar{M}_n$</td>
<td>$\bar{M}_w$</td>
<td>$\bar{M}_n$</td>
</tr>
<tr>
<td>GPC</td>
<td>Weighed</td>
<td>Measured</td>
<td>Theoretical</td>
</tr>
<tr>
<td>16.8</td>
<td>1.700</td>
<td>3.200</td>
<td>31,000</td>
</tr>
<tr>
<td>39.6</td>
<td>4.500</td>
<td>5.700</td>
<td>41,200</td>
</tr>
<tr>
<td>61.5</td>
<td>7.200</td>
<td>7.800</td>
<td>40,500</td>
</tr>
<tr>
<td>75.5</td>
<td>7.900</td>
<td>9.400</td>
<td>44,800</td>
</tr>
</tbody>
</table>

Table 4.4.3: Overall parameters for PS/PDMS blends calculated from GPC/LALLS results. All theoretical results are based on molecular weight values obtained from homopolymer GPC RI traces, using the "GPC/LALLS" column calibration described in Subsection 4.4.2.
<table>
<thead>
<tr>
<th>Copolymer</th>
<th>PS Component</th>
<th>PDMS Component</th>
<th>Overall Copolymer</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$M_n$</td>
<td>$\overline{M}_w$</td>
<td>$M_n$</td>
</tr>
<tr>
<td>B12</td>
<td>8,300</td>
<td>65,400</td>
<td>5,300</td>
</tr>
<tr>
<td>B12</td>
<td>9,500</td>
<td>65,000</td>
<td>6,300</td>
</tr>
<tr>
<td>B13</td>
<td>4,700</td>
<td>66,100</td>
<td>5,900</td>
</tr>
<tr>
<td>B16</td>
<td>39,700</td>
<td>54,300</td>
<td>13,400</td>
</tr>
<tr>
<td>B20</td>
<td>10,700</td>
<td>17,400</td>
<td>2,700</td>
</tr>
<tr>
<td>B20</td>
<td>12,700</td>
<td>17,100</td>
<td>3,200</td>
</tr>
<tr>
<td>B21</td>
<td>3,700</td>
<td>15,300</td>
<td>7,600</td>
</tr>
<tr>
<td>B21</td>
<td>3,200</td>
<td>14,400</td>
<td>6,900</td>
</tr>
<tr>
<td>B22</td>
<td>26,900</td>
<td>43,900</td>
<td>11,300</td>
</tr>
<tr>
<td>B22</td>
<td>27,300</td>
<td>44,600</td>
<td>11,900</td>
</tr>
</tbody>
</table>

Table 4.4.4: Overall parameters for PS/PDMS copolymers calculated from GPC/LALLS results.
<table>
<thead>
<tr>
<th>Blend Composition (% PS)</th>
<th>Random Error in H</th>
<th>Actual Error in H</th>
</tr>
</thead>
<tbody>
<tr>
<td>20.5</td>
<td>0.05</td>
<td>0.02</td>
</tr>
<tr>
<td>40.2</td>
<td>0.02</td>
<td>0.03</td>
</tr>
<tr>
<td>59.5</td>
<td>0.03</td>
<td>0.04</td>
</tr>
<tr>
<td>75.9</td>
<td>0.02</td>
<td>0.06</td>
</tr>
</tbody>
</table>

Table 4.4.5: Estimated random errors in the calculated values of H for PS/PDMS blends, together with the errors actually seen.

<table>
<thead>
<tr>
<th>Copolymer</th>
<th>Mean Value of H</th>
<th>Estimate of Single Run Error in H</th>
<th>Random</th>
<th>Systematic</th>
<th>Overall</th>
</tr>
</thead>
<tbody>
<tr>
<td>B12</td>
<td>0.82</td>
<td>0.03</td>
<td>0.02</td>
<td>0.03</td>
<td></td>
</tr>
<tr>
<td>B13</td>
<td>1.01</td>
<td>0.02</td>
<td>0.02</td>
<td>0.02</td>
<td></td>
</tr>
<tr>
<td>B16</td>
<td>0.25</td>
<td>0.04</td>
<td>0.02</td>
<td>0.04</td>
<td></td>
</tr>
<tr>
<td>B20</td>
<td>0.22</td>
<td>0.16</td>
<td>0.02</td>
<td>0.16</td>
<td></td>
</tr>
<tr>
<td>B21</td>
<td>0.38</td>
<td>0.05</td>
<td>0.02</td>
<td>0.06</td>
<td></td>
</tr>
<tr>
<td>B22</td>
<td>0.23</td>
<td>0.04</td>
<td>0.02</td>
<td>0.04</td>
<td></td>
</tr>
</tbody>
</table>

Table 4.4.6: Estimated errors in calculated values of H for PS/PDMS copolymers.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>GPC/LALLS</th>
<th>Static LALLS</th>
</tr>
</thead>
<tbody>
<tr>
<td>P</td>
<td>0</td>
<td>1,500</td>
</tr>
<tr>
<td>Q</td>
<td>1,500</td>
<td>2,100</td>
</tr>
<tr>
<td>$\overline{M_w}$</td>
<td>31,600</td>
<td>29,900</td>
</tr>
<tr>
<td>$\overline{M_w}_{PS}$</td>
<td>14,800</td>
<td>19,200</td>
</tr>
<tr>
<td>$\overline{M_w}_{PDMS}$</td>
<td>15,100</td>
<td>20,400</td>
</tr>
<tr>
<td>H</td>
<td>0.38</td>
<td>0.49</td>
</tr>
</tbody>
</table>

Table 4.4.7: A comparison of the parameters obtained using GPC/LALLS with those obtained using static LALLS for copolymer B21.
<table>
<thead>
<tr>
<th>Copolymer</th>
<th>PS Component</th>
<th>PDMS Component</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$M_n$</td>
<td>$M_n$ (Taylor)</td>
</tr>
<tr>
<td>B12</td>
<td>22,600</td>
<td>45,700</td>
</tr>
<tr>
<td>B12</td>
<td>28,500</td>
<td>45,700</td>
</tr>
<tr>
<td>B13</td>
<td>14,000</td>
<td>45,700</td>
</tr>
<tr>
<td>B13</td>
<td>13,800</td>
<td>45,700</td>
</tr>
</tbody>
</table>

Table 4.4.8: Results of analysing B12 and B13 as blends.
Table 4.4.9: P and Q parameters obtained using block copolymer equations as compared to the measured values.
CHAPTER 5

DISCUSSION
Section 5.1

Summary of PS/PDMS Results

5.1.1. Refractive Index Increment Results

Refractive index increments of PS and PDMS homopolymers, a PS/PDMS blend, and a PS/PDMS copolymer were measured in different solvents.

For both the blend and the copolymer, there appeared to be a linear relationship between refractive index increment and composition (equation 2.2.9). This result is important in copolymer light scattering theory and when using an RI detector as part of a system investigating blend or copolymer composition. The only case where the relationship appeared doubtful was that of the copolymer in toluene.

The variation of refractive index increments with molecular weight was investigated for PDMS in TTCE. There was a change of less than 2% in going from an $M_w$ of 10,000 to an $M_w$ of 100,000. Within the molecular weight range considered in this study the variation appeared negligible.

5.1.2. Static LALLS Results

Homopolymer LALLS runs were performed in different solvents to obtain $M_w$ values for PS and PDMS samples. The values agreed, within experimental error, from solvent to solvent.

Apparent molecular weight values were obtained for a PS/PDMS blend in three different solvents. These values were then used in equation 2.2.12 to obtain "true" molecular weight and heterogeneity values. The values of $Q$ and $M_{PS}^\text{PS}$ were in good agreement with theory (note that the good $M_w$ value obtained is because one of the solvents used masked the PDMS component almost completely), but the other values were in less good
agreement. Although the shape of the curve represented by equation 2.2.12 was in good agreement with theory, errors were actually greater than anticipated (Figure 4.2.1).

LALLS was also used to obtain molecular weight and heterogeneity values for copolymer B21.

5.1.3. GPC Analyses

Viscometry was used to show that TTCE was a good solvent for both PS and PDMS. This suggested that GPC should proceed in a straightforward manner.

GPC traces were compared from the two concentration detectors (RI and IR) for PDMS homopolymer runs. Good agreement was obtained at the high molecular weight and of the chromatograms, but poor agreement was reached at the low molecular weight end, which showed a longer tail on the IR trace. This particularly affected the $M_n$ values obtained.

PS/PDMS blends were fully analysed using the dual detector GPC system to produce an MWD for each component, and an overall blend composition. So long as the proportion of PS was not too low ($\leq 30\%$), the analysis gave good $M_w$ and overall composition values, but the $M_n$ values produced were all too low. At low % PS the calculated MWD of the PS component became considerably distorted, so that its $M_w$ value was incorrect as well as its $M_n$ value. These errors, and the $M_n$ errors observed for all the samples, are thought to be due to detector inconsistencies.

The same experimental set up was used to look at the PS/PDMS copolymers. The overall compositions obtained were in good agreement with those of Taylor\textsuperscript{89} and the results obtained previously using two GPC runs each with a single IR detector set at a different wavelength. The $M_n$ values were in poor agreement with those of Taylor, but especially so in the case of copolymers
B12, B13, and B21. The $M_w$ values for these samples were also in poor agreement with those of Taylor, but very good agreement was obtained for the other samples. Since Taylor's method of calculation involved the assumption that no PDMS homopolymer was present in the samples, this suggests that B12, B13, and B21 were, to some extent, blends. In the case of B12 and B13 the large observed variation of composition with molecular weight (Figure 4.3.7) supports this view. B16, B20, and B22 are believed to be "good" copolymers, and the results of Taylor appear correct for these samples.

5.1.4. GPC/LALLS Analyses

The GPC columns were calibrated by using GPC/LALLS to obtain an $M_w$ value, and its corresponding elution volume, for each of a series of homopolymer samples. The slopes of both the PS and PDMS calibration curves were calculated from viscometry results (assuming equation 2.3.5) although this should not have been necessary if sufficient GPC/LALLS runs had been performed.

A series of blends were run and analysed as "unknown copolymers" using the GPC/LALLS method developed for this project and described in Section 2.6. This yields a heterogeneity parameter $H_i$ (which should be unity for blends) at each elution volume, and overall heterogeneity parameters $P$, $Q$, and $H$ as well as the molecular weight and average composition data. In the case of blends it was possible to work out theoretical errors in $H_i$ caused by assumptions made in their calculation. These errors were due to ignoring $P_1$ in equation 2.6.6 and using the wrong interpolation method in calculating the molecular weight $M_1$ at each elution volume. They were considerably less than the errors actually observed. The main errors were therefore experimental. The overall results were generally better than those obtained using static LALLS, the value of $H$ being very close to the theoretical
blend value of unity in each case. Errors in component molecular weights were about the same size as those obtained using a dual concentration detector blend analysis. As before, poor results were obtained at low % PS.

Copolymers were run and analysed in exactly the same way. This produced the following data about the samples:

1. B13 is a homopolymer blend of high molecular weight PS with low molecular weight PDMS. This is shown from the value of H (1.01), and the shape of the sample's composition curve (Figure 4.4.9). The $M_w$ value obtained from Taylor's data using a blend assumption supports this interpretation.

2. B12 is a homopolymer blend of high molecular weights PS with low molecular weights PDMS and some copolymer. The evidence used, and the supporting evidence, are the same as for B13.

3. B21 is a high molecular weight copolymer together with a blend of lower molecular weight homopolymers. This is shown by the variation of $H_i$ with molecular weight. Supporting evidence is the relatively large value of $H$ from both this analysis (0.38) and static LALLS (0.49) and the disagreement between the dual concentration detector molecular weight results and those calculated from Taylor's results assuming a pure copolymer sample.

4. B16 and B22 are copolymers of a lower compositional heterogeneity, as shown by the low $H$ values obtained (0.25 and 0.24 respectively).
Use of the $M_n$ results obtained by Taylor with the GPC/LALLS results shows that the equations for random coupling statistics fit in with the results obtained.

5. B20 has low compositional heterogeneity, but experimental error was too high to obtain accurate results for this sample.

An alternative way of looking at the data at each elution volume is, instead of looking at $H_i$ values, to look at $\bar{M}_A$, $\bar{M}_B$, $\bar{M}_A$, $\bar{M}_B$, and $\bar{M}_A$ values (Figures 4.4.5 - 4.4.8 and 4.4.10 - 4.4.15). For a compositionally homogeneous copolymer

$$\bar{M}_A = \bar{M}_A$$

$$\bar{M}_B = \bar{M}_B$$

For a blend, however

$$\bar{M}_A = M_i$$

$$\bar{M}_B = M_i$$

Looking at the $\bar{M}_A$ and $\bar{M}_B$ values possibly gave a more physically meaningful picture of heterogeneity than looking at $H_i$ values.

Errors in $H$ could, for PS/PDMS samples, be considered as consisting of a random error of 210 in $Q$ together with an absolute (in terms of runs for a particular sample) error of 0.02 in $H$. At $M_w$'s of less than 25,000 the LALLS response was too poor to get consistent results.
5.1.5. **Overview of PS/PDMS Results**

The GPC/LALLS results obtained here have yielded a considerable amount of information about the samples investigated, and what supporting evidence is available suggests that the method was giving a correct interpretation.

The main problem encountered concerned the concentration detectors used, as there was definitely a discrepancy between the two. This has had an effect on all the results. The $M_n$ results were especially affected, but at low % PS there was also a marked effect on the composition calculations which affected all the parameters calculated. It would be useful to get accurate $M_n$ values from the analysis, as in this case independently obtained $M_n$ data had to be used to check block copolymer random coupling statistics. It is possible that the problem was connected with the IR cell used, and a simple change of cell would have solved it.

The system of PS/PDMS copolymer in TTCE is in many ways ideal for the GPC/LALLS method. PS and PDMS both have similar GPC column calibrations (Figure 4.4.1) and TTCE has a refractive index between those of the two components, which are widely different, so that light scattering due to compositional heterogeneity is significant. For other systems the method may not be so straightforward.
Section 5.2

Molecular Weight Calibrations

5.2.1. Method of Obtaining Homopolymer Calibrations

Since the technique depends on taking LALLS readings at each elution volume, GPC/LALLS should be the method of column calibration most consistent with use in this system. Sufficient calibration points should be obtained to avoid the necessity of making assumptions about the calibration slope (as was necessary in this work), but it should normally be satisfactory to express the results obtained as a "correction" to some standard calibration obtained using narrow MWD standards.

5.2.2. The \( P_i = 0 \) Assumption

In the case of PS/PDMS copolymers in the molecular weight range 10,000-100,000 the two component column calibrations are very similar in TTCE (see Figure 4.4.1), and the assumption of \( P_i = 0 \) at each elution volume causes no significant errors. When the two component calibrations are significantly different, however, the assumption becomes less valid, and this could have a significant effect on the errors produced.

To illustrate the point, consider the calibrations of polystyrene/polybutadiene (PS/PBD) and polystyrene/polymethylmethacrylate (PS/PMMA) blends in THF. Table 5.2.1 shows the relationship between the molecular weight of the two components at the \( i \)th elution volume interval in each case. Also shown is the molecular weight of the non-PS component at an elution volume corresponding to \( M_{PSi} = 30,000 \). The \( M_{PDMSi} \) value at this elution volume is slightly lower than 30,000, the \( M_{PMMAi} \) value slightly higher, and the \( M_{PBDi} \) value much lower, corresponding to a significantly different calibration. A comparison of the theoretical errors in \( H_i \)
due to ignoring $P_1$ at $M_{PS1} = 30,000$, is shown in Figure 5.2.1.

(No parameters other than component molecular weights have been changed from curve to curve.) It can be seen that for components having widely differing calibrations the error in $H_1$ is far more significant. The absolute error will be less for copolymers, but, for copolymers where the requirement of similar component calibrations cannot be met, the value of this method may be somewhat limited.

Possible changes in the analysis to account for this error are discussed in Subsection 5.3.2.

5.2.3. The Interpolation Method for Determining $M_i$ Values

The molecular weight $M_i$ of a copolymer at each elution volume is calculated according to equation 2.5.6, representing the method of linear interpolation along a logarithmic scale suggested by Cramond et al.\textsuperscript{100} and Runyon et al.\textsuperscript{28}:

$$\log M_i = W_i \log M_{Ai} + (1-W_i) \log M_{Bi}$$

This equation, however, is intuitive rather than rigorous. Other methods of interpolation, such as that used by Chang\textsuperscript{84,85}, may be more correct:

$$\frac{1}{M_i} = \frac{W_i}{M_{Ai}} + \frac{(1-W_i)}{M_{Bi}} \quad (5.2.1)$$

Similarly, it has already been shown that, for a blend, interpolation along a linear scale is the most appropriate method for use in this analysis:

$$M_i = W_i M_{Ai} + (1-W_i) M_{Bi} \quad (5.2.2)$$

As shown in Figure 5.2.2, the errors caused when calculating blend $H_1$ values using equation 2.5.6 instead of equation 5.2.2
are greater when the molecular weight calibrations of the two components are appreciably different. For copolymers, similarly, the choice of interpolation method should be most important when this is so. The example of the PS/PBD calibrations is therefore considered, the effect of the various methods being shown in Table 5.2.2. This shows that the effect of the interpolation method is insignificant unless compositional heterogeneity is very small, i.e. too small to be detected except possibly in the case of very high molecular weight samples. This suggests that equation 2.5.6 may well be satisfactory even when the GPC separation mechanism is questionable, providing that the two component calibrations are not too dissimilar.

An important consideration is the possible presence of interactions in copolymers which are absent in homopolymers. A particular cause for concern is that interactions between dissimilar copolymer segments may mean that the sizes of the segments may not be directly comparable with those of the corresponding homopolymers. This is generally only important when there are many heterocontacts between unlike segments, as is the case for random copolymers but not for block copolymers. Graft copolymer Mₑ values cannot be calculated directly from interpolation because molecular structure effects the relationship between molecular size and weight.

One way round problems encountered using interpolation techniques would be to make use of an on line viscometer for molecular weight monitoring, although this would involve making universal calibration assumptions. A viscometer which measures the pressure drop through a capillary is likely to be the most suitable for modern GPC systems. Unfortunately such an instrument is not available commercially at present.
The effect of different blend component calibration relationships on the error in $H_i$ due to ignoring $P_i$ when $M_{PSi} = 30,000$. 

Figure 5.2.1.
The effect of different blend component calibration relationships on the error in $H_i$ due to incorrectly calculating $M_i$ values when $M_{PSi} = 30,000$. 

Figure 5.2.2.
<table>
<thead>
<tr>
<th>Type of Blend</th>
<th>Relationship between component molecular weights at the ( i )th elution volume interval</th>
<th>Molecular weight of 2nd component when ( M_{PSi} = 30,000 )</th>
<th>Solvent for which the relationship is valid</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>PS/PDMS</td>
<td>( 6.4 \times 10^{-3} (M_{PSi}^{'} \cdot 1.75 = 2.9 \times 10^{-3} (M_{PDMSi}^{'} \cdot 1.84 )</td>
<td>27,900</td>
<td>TTCE</td>
<td>This work</td>
</tr>
<tr>
<td>PS/PMMA</td>
<td>( 1.68 \times 10^{-3} (M_{PSi}^{'} \cdot 1.69 = 9.3 \times 10^{-4} (M_{PMMAi}^{'} \cdot 1.72 )</td>
<td>35,300</td>
<td>THF</td>
<td>Ref. 19</td>
</tr>
<tr>
<td>PS/PBD</td>
<td>( M_{PSi}^{'} = 1.75 M_{PBDi}^{'} )</td>
<td>17,100</td>
<td>THF</td>
<td>Ref. 34</td>
</tr>
</tbody>
</table>

Table 5.2.1: The relationship between blend component molecular weights assumed in evaluating the curves shown in Figures 5.2.1 and 5.2.2.
Table 5.2.2: The effect of using different molecular weight interpolation methods on a copolymer following the PS/PBD calibration relationship \( (M_{PS_i'} = 1.75 M_{PBD_i'}) \) at an elution volume corresponding to \( M_{PS_i'} = 30,000 \) and \( M_{PBD_i'} = 17,100 \). Note that the refractive index increments used in the calculation were those used in Figures 5.2.1 and 5.2.2, i.e. those of PS and PDMS in TTCE.

<table>
<thead>
<tr>
<th>Interpolation Method</th>
<th>Copolymer Molecular Weights</th>
<th>Change in ( H_i ) from the value obtained using linear interpolation along a log scale</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0% PS</td>
<td>20% PS</td>
</tr>
<tr>
<td>Log Scale</td>
<td>17,100</td>
<td>19,200</td>
</tr>
<tr>
<td>Linear Scale</td>
<td>17,100</td>
<td>19,700</td>
</tr>
<tr>
<td>Chang</td>
<td>17,100</td>
<td>18,800</td>
</tr>
</tbody>
</table>
Section 5.3

Light Scattering Considerations

5.3.1. The Interpolation Method for Determining \( v_i \) Values

The whole of copolymer light scattering theory is based on the assumption that copolymer refractive indices vary linearly with composition:

\[
v = W v_A + (1-W) v_B
\]  

(2.2.9)

Although the theory fits best to block (or graft) copolymers \(^{26}\), the relationship has also been verified for random copolymers \(^{105}\). It does not appear, therefore, that this need normally be a serious consideration for any copolymer type.

5.3.2. Solvent Refractive Indices

The greatest accuracy in determining the compositional heterogeneity parameter \( Q \) using light scattering is obtained when the condition \( v = 0 \) can be satisfied \(^{55}\). Similarly, in the GPC/LALLS analysis, the greatest accuracy in determining both \( Q_i \) and \( H_i \) values is obtained when \( v_i = 0 \). As an illustration of this effect on the theoretical errors (due to ignoring \( P_i \)) in \( H_i \), the case of PS/PDMS and of PS/PMMA blends in various solvents is shown in Figure 5.3.1. The molecular weight calibration relationships assumed are those given in Table 5.2.1. (i.e. no account has been taken of the variation in the relationship from solvent to solvent), and the component refractive index increment values used are given in Table 5.3.1. Errors in \( H_i \) can be seen to be very solvent dependent, zero (theoretical) error values being obtained at a blend composition corresponding to \( v_i = 0 \). In the case of the PS/PMMA blend, where \((v_A - v_B)\) values are less than for PS/PDMS blends (about
0.09 cm$^{-1}$ as opposed to 0.18 cm$^{-1}$ for PS/PDMS), the choice of solvent can be seen to be more critical. Considerably larger errors than those for either of those blends would be expected for PS/PBD blends in THF.

One possible solution to the problem would be to replace $H_i$ by a parameter $H_i'$ which has a value of zero for a homogeneous copolymer and unity for a blend after $P_i$ has been taken into account. One could, for instance, "correct" $H_i$ by a factor $F_i$ defined as:

$$F_i = 1 - \frac{2 \nu_i P_i, \text{max}}{(\nu_i - \nu_B)Q_i \text{ max}}$$

where $P_i, \text{max} = W_i (1-W_i) (M_{\text{Ai}} - M_{\text{Bi}}')$ and $Q_i, \text{max} = W_i (1-W_i) [(1-W_i)M_{\text{Ai}}' + W_i M_{\text{Bi}}']$.

Similarly, corrections could be made to take account of the fact that $M_i$ should be replaced by $\overline{M_i}$, in the blend situation, but this effect is very small.

There are several reasons why the use of mathematical corrections in preference to reconsidering the choice of solvent is to approach the problem from the wrong end:

1. When $(M_{\text{Ai}} - M_{\text{Bi}}')$ and $(\nu_i - \nu_{\text{Ai}})$ are of opposite sign (e.g. for PS/PMMA copolymers in THF), $M_i$ can sometimes be less than $M_i$ when $P_i$ is non-zero (see Figure 2.2.1). This would give negative $H_i'$ signals, and make interpretation ambiguous.

2. Since $H_i'$ generally contains an unknown contribution from $P_i$ it would not be possible to use it to calculate overall heterogeneity parameters without using further assumptions.

3. The method, regardless of refinements, is
essentially measuring \((M_i^* - M_i)\) values. Unless \(v_i\) is very small, \((M_i^* - M_i)\) will be very difficult to measure accurately because of the limited sensitivity of the LALLS photometer and any inaccuracies in measured \(M_i\) values.

For the above reasons it appears that the best solution to the problem is to find a solvent whose refractive index lies between those of the two sample components. The use of a correction such as \(F_i\) is not excluded, however, and the combination of \(F_i\) values and \(H_i'\) values may well prove a more useful output than just the "uncorrected" \(H_i\) values presented in this work. It is not clear at this stage whether \(H_i\) or \(H_i'\) values would be more useful in calculating overall heterogeneity parameters. At present it appears best simply to be aware of the errors and to minimise them as far as possible in the experimental method.

5.3.3. Copolymer Component Refractive Indices

It was observed in Subsection 5.3.2 that the choice of solvent becomes more critical the smaller the magnitude of \((v_A - v_B)\) becomes. Assuming a solvent having a suitable refractive index is found, the magnitude of \((v_A - v_B)\) makes no difference to the theoretical errors in the \(H_i\) values. However, it does affect the magnitude of the LALLS signal due to heterogeneity, and hence the sensitivity of the technique.

PS/PMMA copolymers have \((v_A - v_B)\) values about half the magnitude of those for PS/PDMS copolymers

\[
\begin{align*}
(v_{PS} - v_{PMMA}) & \approx 0.09 \text{ cm}^3 \text{ g}^{-1}, & v_{PS} - v_{PDMS} & \approx 0.18 \text{ cm}^3 \text{ g}^{-1}, \\
\end{align*}
\]

and this corresponds to a PS/PMMA LALLS signal due to heterogeneity one quarter the magnitude of the corresponding PS/PDMS signal. As the lower molecular weight limit for PS/PDMS copolymers appears to be about 25,000, a molecular weight of at least
100,000 should be needed for reproducible PS/PMMA results. PS/PBD copolymers would have to be of an even higher molecular weight.

For copolymers in a single solvent system, \((\psi_A - \psi_B)\) is almost independent of solvent. However, Tuzar et al. \(^{106}\) overcame this problem by using mixed solvents, measuring all refractive indices after dialysis equilibrium between solvent and solute had been attained. Use of mixed solvents should be possible for the GPC/LALLS copolymer characterisation method, but this may complicate the GPC and concentration detector side of the analysis (in particular, it is likely to reduce the number of windows for use with a spectroscopic detector).

5.3.4. **Overall Choice of Solvent**

From the above discussion, and general considerations, one can conclude that there are several factors (not all related to light scattering) which will affect the choice of solvent. The following conditions are desirable:

1. The solvent should be compatible with the concentration detectors used (e.g. there must be suitable windows in the case of spectroscopic detectors).

2. The refractive index increment of the copolymer in the chosen solvent should be small. Component refractive index increments of opposite signs are highly desirable.

3. The magnitude of \((\psi_A - \psi_B)\) should be large.

It is essential that condition 1 is satisfied. This will be examined further in Section 5.4.

Very large errors can result if condition 2 is not satisfied. However, their magnitude depends upon whether the two copolymer
components have similar column calibrations. For instance, if both these calibrations are identical, there will be no theoretical errors due to ignoring $P_1$, regardless of whether condition 2 is satisfied. Even in this case the condition is likely to be important because it affects the sensitivity of the technique.

The importance of condition 3 depends on the molecular weight of the copolymer. This work suggests that the necessary condition is

$$(\nu_A - \nu_B)^2 \times \bar{M}_w > 1,000$$

so long as condition 2 is satisfied.

It is easy to see that careful choice of solvent is essential to this type of analysis.
Figure 5.3.1. The effect of using solvents with different refractive indices on blend $H_1$ errors, due to ignoring $P_i$, at elution volumes corresponding to $M_{PSi} = 30,000$. BB refers to bromobenzene.
Table 5.3.1: Homopolymer refractive increment values used in evaluating the curves shown in Figure 5.3.1.
Section 5.4

Concentration Detectors

5.4.1. Selectivity of Detectors

For any copolymer GPC work using dual concentration detectors it is essential that, overall, each detector behaves differently in its response to the two copolymer components.

For the GPC/LALLS analysis considered here, it is very likely that an RI detector will be one of those chosen. Light scattering considerations dictate that the two copolymer components must have different refractive indices in solution. What is more, the chosen solvent should ideally give a negative $\nu$ value for one component and a positive $\nu$ value for the other. Thus, it is inevitable that, if this condition is satisfied, each copolymer component will oppose the other in contributing to an RI trace. An RI detector can therefore be used with a second concentration detector which is either selective toward one of the components (e.g. a spectroscopic detector) or universal (e.g. an evaporative analyser, crystal mass detector, or densimeter). An IR detector of the type described by Mori et al. appears particularly useful as its high sensitivity allows much wider transmission windows than normally experienced with IR detectors. However, in practice, choice of concentration detectors is likely to be limited by what is commercially available.

There may be occasions when the concentration detector combination does not include an RI detector. Examples of this would be when two detectors of a higher sensitivity could be found or when the use of a single spectroscopic detector was felt preferable to two separate concentration detectors (see Subsection 5.4.2). However, in many circumstances, the process of choosing suitable concentration detectors may consist of no more than choosing a second detector for use in conjunction with an RI detector.
5.4.2. **Inconsistencies Between Detectors**

The main problem encountered in the present work has been due to inconsistencies in the responses of the two concentration detectors, affecting the low molecular weight end of the chromatograms. It is quite possible, however, that the problem could have been solved quite simply by changing the IR detector cell.

Using marker peak positions to indicate the delay between detectors appears perfectly satisfactory (judging by the good agreement between homopolymer \( M_z \) values obtained in this work). There may be something to be said, however, for using homopolymer peak positions to obtain this delay because, in the final analysis, it is polymers that are being investigated.

The use of a single spectroscopic detector may have its advantages with regard to detector inconsistencies, although it did not seem satisfactory for this study. A single concentration detector method preferable to using double runs at separate wavelengths would be to use a Fourier transform IR \(^{112,113}\) or rapid scanning UV spectrophotometer \(^{114}\). Such equipment is expensive, however, and, since the LALLS photometer must always exist as a separate detector, the single detector approach can never be fully realised.

Whatever detector system is selected, the use of homopolymer (or possibly blend) runs as a consistency check between the detectors (or detector wavelengths) is strongly recommended if erroneous results are to be avoided.

5.4.3. **Detector Responses in Copolymers**

In calculating composition and concentrations of each elution volume, it is assumed that concentration detector calibrations obtained using homopolymers will be valid for each copolymer component. Mathematically this leads to equations 2.4.1 and 2.4.2 giving, for
each concentration detector, a response signal equal to

\[ r_i = k_A c_{A_i} + k_B c_{B_i} \]  

(5.4.1)

where \( c_{A_i} \) and \( c_{B_i} \) are the concentrations of each component at the \( i \) th elution volume. In each case the calibration constants (\( k_A \) and \( k_B \)) are those measured using homopolymer runs.

It was shown in Subsection 5.3.1 that the relationship should be valid in the case of RI detectors regardless of the type of copolymer. In the case of spectroscopic detectors, however, the assumption is not always valid. Marked deviations from equation 5.4.1 have been observed for UV detectors in the case of random copolymers \(^{80,115}\). The effect is solvent dependent, so careful choice of solvent may overcome the problem \(^{80}\). Although the UV/RI detector combination has been used in the GPC of many styrene-containing block copolymers \(^{28,29,31,32,34,35}\), there is evidence that they, too, sometimes deviate from the desired relationship \(^{81,115}\). There may also be an effect on IR bands. Appreciable shifts have been observed when going from homopolymer spectra to those of random copolymers \(^{116}\). This could possibly cause problems when using IR detectors at fixed wavelength for random copolymer work.

The development of non-spectroscopic detectors \(^{107-110}\) should permit more flexibility when choosing a suitable detector system (although their use does not permit the single concentration detector approach).

By adopting a flexible approach, therefore, it is likely that a suitable detector system may be found even for random copolymers.
Section 5.5

Overall Evaluation

5.5.1. Applicability of the Technique to Different Copolymer Types

The discussion has pointed out several reasons why the technique is best suited to block copolymers, the most significant one relating to the molecular weight interpolation method. However, by use of an on-line viscometer and careful selection of concentration detectors it may be possible to accommodate both graft and random copolymers.

Equation 5.3.3 essentially defines the limits of detection. If it is not satisfied in single solvents, the use of mixed solvents may help. It is also important that the conditions stated in Subsection 5.3.4 can be satisfied, and that detectors can be found that correctly reflect copolymer component concentrations. It is possible that the technique will still be useful for blend/copolymer differentiation even when suitable conditions for reliable overall heterogeneity parameters cannot be obtained.

5.5.2. The Use of Copolymer GPC/LALLS in Relation to Other Techniques

The number of considerations required in setting up a GPC/LALLS system for a new copolymer type dictate that in such a case it cannot be routine. However, once the background work has been done on that copolymer type the technique is very fast, and this is an advantage over all other techniques which look simultaneously at molecular weight and composition distributions. Such techniques depend on cross fractionation of some sort, and this either involves collecting fractions or using a stop flow technique, both of which are time consuming (collecting fractions considerably more so). Cross fractionation techniques potentially provide more detailed information, however.
Considerably more information can be gained using the GPC/LALLS method than from either pure GPC or pure LALLS. It is also considerably faster than pure LALLS (bearing in mind that to gain maximum information from static LALLS at least three separate runs in different solvents are required together with a compositional analysis).

The GPC/LALLS technique is therefore useful when an indication of both molecular weight and composition distributions are required without resorting to the sophistication of cross fractionation techniques. It may also, on occasions, be the most convenient way of measuring compositional heterogeneity.

5.5.3. Suggested Further Work

A particular problem encountered in this work has been the incompatibility of the concentration detectors at the low molecular weight end of the chromatograms. It would be satisfying, therefore, to see suitable detectors selected so that this was not so, in which case it should be possible to check, for instance, block copolymer random coupling statistics without needing any additional information.

The assumption of zero \( P_1 \) values may cause appreciable errors under certain circumstances. It would be useful to investigate the use of alternative assumptions (e.g., a particular type of distribution at each elution volume) to see whether these errors could be reduced.

The technique is not suitable for all types of copolymer in its present form. An investigation of its use on random or graft copolymers (making use of an on-line viscometer) and copolymers whose components have similar refractive index increments in single solvents (by changing over to a mixed solvent system) would potentially extend its applicability.
REFERENCES


