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# Compositional Heterogeneity of Copolymers by Combined GPC and Lalls

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# COMPOSITIONAL HETEROGENEITY OF COPOLYMERS BY COMBINED GPC AND LALLS

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## ABSTRACT

A method for determining the compositional heterogeneity of copolymers is described. A low-angle laser light-scattering (LALLS) photometer is added on-line to a dual-concentration-detector gel-permeation chromatograph (GPC) in order to measure heterogeneity at each elution volume interval. Experimental results for polystyrene-poly(dimethylsiloxane) diblock copolymers and blends are discussed, and these give overall heterogeneity parameters which are in good agreement with theory. The technique shows, however, that some of the samples originally thought to be copolymers were actually blends or contained homopolymer. Both random errors and errors inherent in the analysis are examined. The largest inherent error arises from the assumption that there is no distribution of molecular weights within a single GPC fraction. An alternative to this assumption is described, and its use considerably reduces the inherent errors. All types of error are reduced by selecting a solvent such that the refractive index increment of the copolymer under investigation is small, and the refractive index of the solvent should ideally fall between those of the

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two copolymer components. The accuracy of the technique increases linearly with copolymer molecular weight and the square of the difference in component refractive index increments.

## INTRODUCTION

The characterization of copolymers in terms of molecular weight and composition is complex due to the interdependence of the two distributions. Most solutions to this problem have involved the use of some type of cross-fractionation technique, separating by composition fractions previously separated by size [1-4] or vice versa [5, 6]. Although thorough, this is a very time-consuming exercise, and a preparative scale experiment was required for the earlier measurements of this type. The technique of orthogonal chromatography [7, 8] is a more sophisticated version of cross-fractionation, making use of a switched valve system to link two gel-permeation chromatographs having different mobile phases. Even in this system, however, the stop-flow nature of the experiment makes the time constraint considerable, and the setup is fairly complex.

Stand-alone light scattering can also be used to determine molecular weight and heterogeneity parameters by taking measurements in three solvents having different refractive indices [9-12]. This requires the measurement of several refractive index increments as well as the light-scattering readings.

The system described here is faster than either approach. The composition data obtainable are less complete than those obtained from cross-fractionation but more complete than those from stand-alone light scattering. A dual-concentration-detector gel-permeation chromatography (GPC) system is used to determine a copolymer's molecular weight distribution (MWD) and the variation of its average composition with molecular weight. The addition of a low-angle laser light-scattering (LALLS) photometer allows the measurement of compositional heterogeneity at each molecular weight and also overall heterogeneity parameters.

## COPOLYMER LIGHT SCATTERING

Light scattering is a technique commonly used in determining the weight-average molecular weight $\bar{M}_w$ of polymers from measurements taken in dilute solution. In the case of copolymers, however, sample compositional heterogeneity also contributes to light-scattering readings [13, 14]. Bushuk and

Benoit [9] described copolymer light scattering in terms of the apparent molecular weight $M^*$ calculated by using standard light-scattering equations. For a two-component polymer, assuming a linear relationship between refractive-index increment and composition [14-17], $M^*$ is related to $\bar{M}_w$ by

$$M^* - \bar{M}_w = 2P(\nu_A - \nu_B)/\nu + Q(\nu_A - \nu_B)^2/\nu^2, \tag{1}$$

where $\nu_A$ and $\nu_B$ represent the refractive index increments of the two components, and $P$ and $Q$ are heterogeneity parameters; $P$ is a measure of the molecular weight influence on compositional heterogeneity and $Q$ is an overall measure of the heterogeneity:

$$\begin{aligned} P &= \sum_j c_j M_j (W_j - W) / \sum_j c_j \\ &= 1/2[(1 - W)(\bar{M}_w - \bar{M}_{wB}) - (\bar{M}_w - \bar{M}_{wA})], \end{aligned} \tag{2}$$

$$\begin{aligned} Q &= \sum_j c_j M_j (W_j - W)^2 / \sum_j c_j \\ &= W(1 - W)(\bar{M}_{wA} + \bar{M}_{wB} - \bar{M}_w), \end{aligned} \tag{3}$$

where $c_j$ is the concentration of all molecules of type $j$, $M_j$ is their molecular weight, and $W_j$ is their composition, while $W$ is the overall composition, and $\bar{M}_{wA}$ and $\bar{M}_{wB}$ are the weight-average molecular weights of the two components.

## COPOLYMER GPC

### Use of Dual Concentration Detectors

The use of two (at least partially) selective concentration detectors on a GPC system allows the calculation of copolymer composition at each elution volume interval [18-23]. Such a calculation would normally assume that each detector has a linear response for each component equal to that for the corresponding homopolymer and independent of molecular weight. Appreciable deviations from these assumptions would only be likely at low molecular weight [22] or for copolymers having short sequence lengths (e.g., random copolymers) [24-26].

### MWD Calibration

GPC separates polymer molecules according to their size in solution (usually assumed to be the hydrodynamic volume), and some sort of column calibration is normally necessary to convert elution volume to molecular weight. In the case of copolymers, the molecular weight $M_i$ at each elution volume is dependent on composition. For block copolymers, a good approximation to $M_i$ may normally be obtained by interpolating between the two component homopolymer calibrations [18, 27, 28]. In this work the method of Runyon et al. [18] has been employed (interpolation along a logarithmic scale), valid provided the two homopolymer calibrations are not vastly different and there are no strong interactions between copolymer blocks (if these conditions are satisfied, all methods should give similar results). On occasions where such calculations are unreliable, the addition of an on-line viscometer [29] to determine molecular weight may be more appropriate.

Component homopolymer calibrations can be made by using narrow-MWD standards of known molecular weight. Because these are unavailable for most polymer types, a universal calibration procedure [30] is frequently used to convert from one polymer type to another. A more direct approach, however, is to use on-line LALLS, acting as a molecular-weight detector [31], to calibrate for each homopolymer type [17, 32]. This method involves the use of a range of samples covering the molecular weight range. For each sample a best-fit linear calibration (appropriate only for that sample), with each point weighted according to both the concentration and LALLS detector response, is constructed from a GPC/LALLS run. From such a run an $\bar{M}_w$ value and its position on such a calibration may be calculated. Only this single point, taken from the (accurate) center of the distribution, is used from each sample calibration. Thus a series of $\bar{M}_w$ values, and their corresponding elution volumes, can be used to construct an overall column calibration appropriate for that particular polymer type.

## COPOLYMER GPC/LALLS

### Calculation Procedure

The copolymer GPC/LALLS setup has a dual concentration system with the addition of a LALLS detector. The two concentration detectors give a value for average copolymer composition $W_i$ at each elution volume interval $i$. This value may in turn be used to calculate the corresponding refractive index increment $\nu_i$ by assuming a linear relationship between $\nu_i$ and $W_i$.

LALLS as a GPC detector is usually used to determine polymer molecular weight $M_i$ at elution volume $V_i$ [31]. For a copolymer, an apparent molecular weight $M_i^*$ may be similarly calculated from the previously determined value of $\nu_i$. From Eq. (1), $M_i^*$ may be related to $\bar{M}_{wi}$, the weight-average molecular weight of the molecules eluting at $V_i$, according to

$$M_i^* - \bar{M}_{wi} = 2P_i(\nu_A - \nu_B)/\nu_i + Q_i(\nu_A - \nu_B)^2/\nu_i^2, \tag{4}$$

where $P_i$ and $Q_i$ are the heterogeneity parameters for those molecules emerging at $V_i$.

If the calibration of the two copolymer components is not too different, $\bar{M}_{wi}$ can be approximated to $M_i$, the value obtained from interpolating between the two component calibrations, and the term $P_i$ can be ignored due to the narrow MWD within each fraction (an alternative to ignoring $P_i$ is discussed in the following section). A value of $Q_i$ may, therefore, be calculated for each value of $V_i$. A parameter $H_i$, varying from 0 to 1, may also be defined by comparing $Q_i$ with its maximum possible value (that for a homopolymer mixture):

$$H_i = Q_i/\ W_i(1 - W_i)[(1 - W_i)M_{Ai}' + W_iM_{Bi}'] \ , \tag{5}$$

where $M_{Ai}'$ and $M_{Bi}'$ are the homopolymer molecular weights which would elute at $V_i$. Since a narrow MWD at each elution volume interval is assumed, both $\bar{M}_{wi}$ and its number-average counterpart, $\bar{M}_{ni}$, can be taken as $M_i$. This allows the calculation of the molecular weights of the individual components:

$$\bar{M}_{wiA} = W_iM_i + Q_i/W_i, \tag{6}$$

$$\bar{M}_{niA} = W_iM_i, \tag{7}$$

$$\bar{M}_{wiB} = (1 - W_i)M_i + Q_i/(1 - W_i), \tag{8}$$

$$\bar{M}_{niB} = (1 - W_i)M_i. \tag{9}$$

Overall component $\bar{M}_w$'s and $\bar{M}_n$'s can be obtained by number- or weight-averaging the appropriate quantities, and overall values for $P$ and $Q$ calculated from Eqs. (2) and (3). An overall $H$ value, comparing $Q$ to its maximum (homopolymer mixture) value, may also be calculated.

### Errors Implicit in the Calculation

The above calculation procedure is perfectly valid so long as there is a narrow MWD at each elution-volume interval, so no fundamental problem should arise if the two copolymer components have similar GPC calibrations. If, however, these two calibrations are significantly different, then the results may be affected because of the theoretical assumptions made. This section examines the resultant errors and suggests a possible method for reducing them.

One type of error arises from the approximations used in calculating $M_i$. Most calculations for block copolymers involve some sort of interpolation technique. Thus the method of Runyon et al. [18] employs interpolation along a logarithmic scale, while that of Chang [27, 28] employs interpolation along a reciprocal scale. Assuming a solvent is chosen such that $\nu_i$ is zero at $W_i = 0.5$ (i.e., $M_{Bi}' = -M_{Ai}'$), then even for the extreme case of $M_{Ai}'/M_{Bi}' = 1.75$ (the calibration relationship for a polystyrene-polybutadiene copolymer in tetrahydrofuran) the difference between the $H_i$ values calculated by the two methods is only 0.01 at $W_i = 0.8$, 0.001 at $W_i = 0.4$, 0.002 at $W_i = 0.6$, and 0.02 at $W_i = 0.8$ [17]. For a more typical case in which the ratio of the component molecular weights is about 1.2:1, the differences will be an order of magnitude less. Thus the calculation method employed in determining $M_i$ does not appear to be an important contributor to errors in $H_i$.

A second type of error arises because the value of $P_i$ at each elution volume interval is not known. The method of calculating $H_i$ described above uses the assumption that $P_i$ is always zero, true only when the two component molecular weights are equal (or when $Q_i = 0$) at elution volume $V_i$. It is possible to calculate the effect of the resultant error on the apparent $H_i$ values for the case of blends, where $H_i$ should always be 1. The solid lines in Fig. 1 show the $H_i$ values calculated for three types of blends having different relative component calibrations. In each case it is assumed that a solvent is chosen that gives a zero $\nu_i$ value at $W_i = 0.5$. Figure 1(a) shows the effect when the two component calibrations are fairly similar (the calibration relationship valid for polystyrene-poly(dimethylsiloxane) in tetrachloroethylene at $M_{Ai}' = 30\,000$ [32]), Fig. 1(b) when the calibrations are fairly typically different (the calibration relationship valid for polystyrene-poly(methyl methacrylate) in tetrahydrofuran at $M_{Ai} = 30\,000$ [30]), and Fig. 1(c) when the calibrations are vastly different (the calibration relationship valid for polystyrene-polybutadiene in tetrahydrofuran at $M_{Ai} = 30\,000$ [33]). The error is seen to become fairly serious in the final case if the composition deviates significantly from that for which $\nu_i = 0$ ($W_i = 0.5$ in this case). Since $P_i$ is roughly proportional to $Q_i$, a 10% error in the apparent $H_i$ of a blend due to ignoring $P_i$ should approximately correspond to a 10% error in the apparent $H_i$ of a lower-hetero-

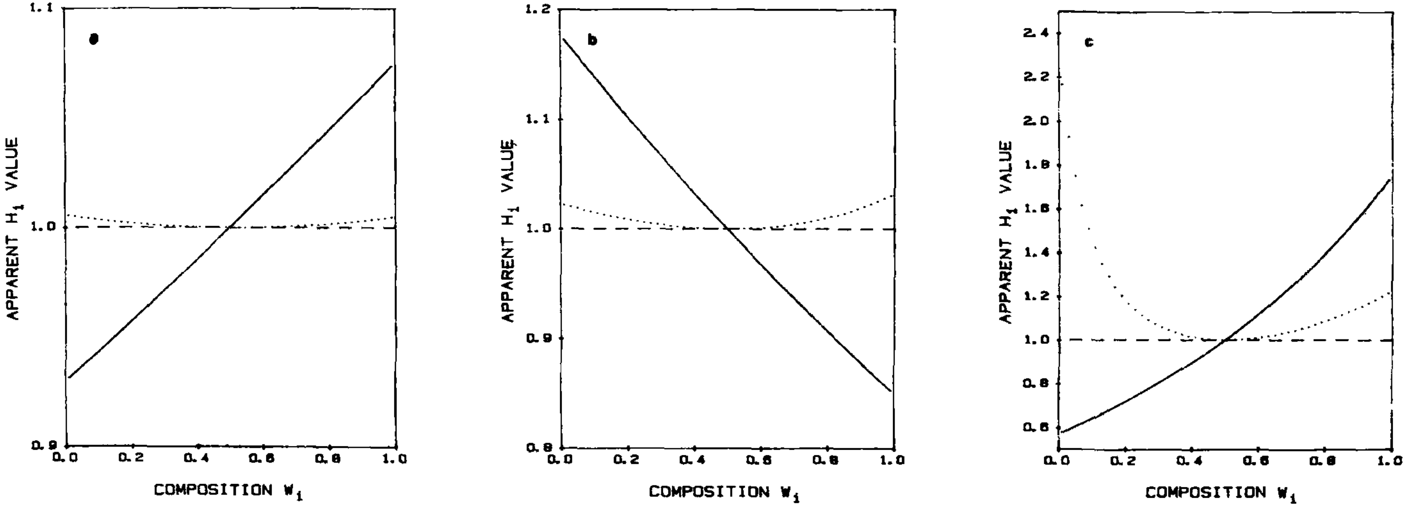

FIG. 1. The effect of assuming that $P_i$ is zero (solid line) or that $P_i$ is given by Eq. (10) (dotted line) on calculated $H_i$ values for blends in a solvent in which $\nu_B = -\nu_A$. The calibration relationships between the two components are (a) $M_{Bi}' = 0.93M_{Ai}'$, (b) $M_{Bi}' = 1.18M_{Ai}'$, and (c) $M_{Bi}' = 0.57M_{Ai}'$. The dashed line represents the theoretical value of $H_i = 1$ in each case.

geneity copolymer, a 5% error in the apparent $H_i$ of a blend to a 5% error in a copolymer, etc.

An alternative to assuming $P_i = 0$ is to estimate the magnitude of $P_i$ with respect to $Q_i$. It is possible to obtain a good approximation to $P_i$ by assuming that, within a single fraction at elution volume $V_i$, a linear relationship exists between molecular weight and composition and the MWD is symmetrical. Manipulation of Eqs. (1) and (2) then leads to

$$P_i = Q_i\,(M_{Ai}' - M_{Bi}')/M_{i,\text{lin}}, \tag{10}$$

where $M_{i,\text{lin}}$ is the $M_i$ value calculated from a linear interpolation between the two homopolymer calibrations, although $M_{i,\text{lin}}$ could be sensibly replaced by the $M_i$ value used for the rest of the analysis.

The above expression may be substituted into Eq. (4), leading to more accurate value of $Q_i$. The resultant calculated $H_i$ values for the blends considered above are shown as dotted lines in Fig. 1. A large improvement is generally observed except in 1(c), where a substantial error remains. It is important to realize, however, that the assumption of a symmetrical distribution around $W_i$ implicit in the estimation of $P_i$ is far from valid for blends except at a composition very close to $W_i = 0.5$. The validity of the assumption is still questionable in the case of true copolymers, but blends represent something of a worst case in this respect, and the improvement in copolymer results is likely to be somewhat larger than that in Fig. 1.

### Selection of Detector/Solvent System

The effect of both $P_i$ and the interpolation technique on the calculated values of $Q_i$ and $H_i$ increases with the magnitude of $\nu_i$. Figure 2 shows the errors in $H_i$ that are due to ignoring $P_i$ or assuming that it may be represented by the relationship given in Eq. (10) for blends having the same calibration relationships as those in Fig. 1. In this case, however, instead of refractive index increments of the components being related by $\nu_B = -\nu_A$, a relationship of $\nu_B = \nu_A/2$ is assumed. Thus, instead of lying between the refractive indices of the two components, the solvent has a refractive index considerably less (or greater) than either. The errors are now much greater for each blend, although the use of Eq. (10) considerably reduces them. It is therefore desirable to have as low a copolymer refractive index increment as possible. A low copolymer refractive index increment is also desirable in reducing random errors in $Q_i$ [34, 35], as the relative contribution of $Q_i$ to the light scattering increases as the magnitude of $\nu_i$ decreases. In general, a solvent whose refractive index falls between those of the two components is ideal.

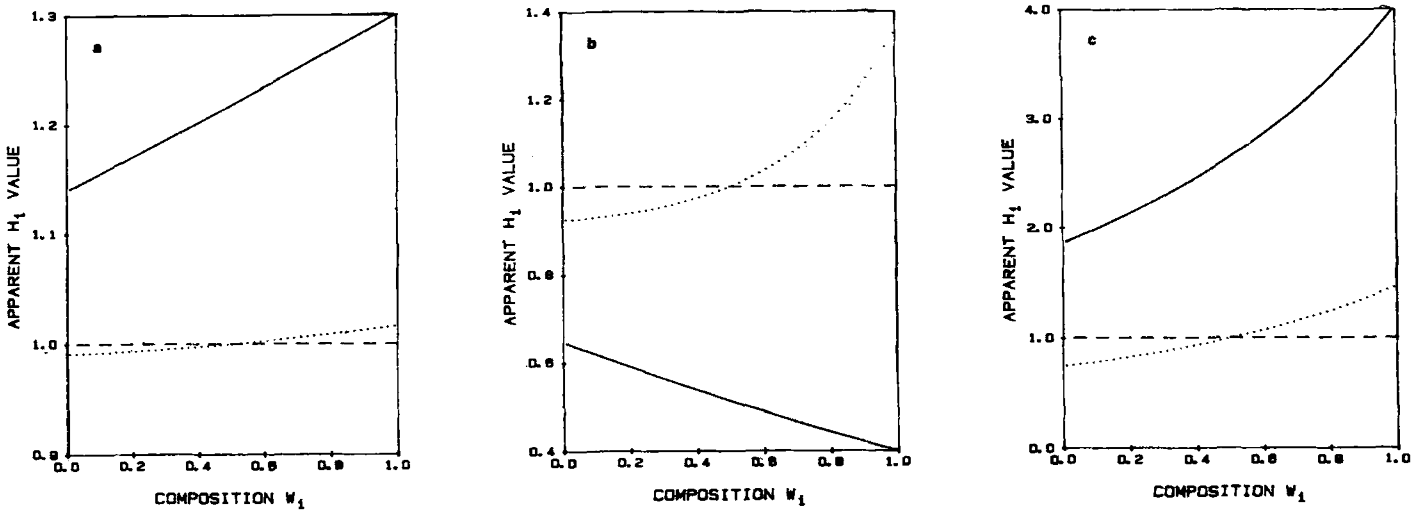

FIG. 2. The effect of assuming that $P_i$ is zero (solid line) or that $P_i$ is given by Eq. (10) (dotted line) on calculated $H_i$ values for blends in a solvent in which $\nu_B = \nu_A/2$. The calibration relationships between the two components are the same as for Fig. 1, i.e., (a) $M_{Bi}' = 0.93M_{Ai}'$, (b) $M_{Bi}' = 1.18M_{Ai}'$, and (c) $M_{Bi}' = 0.57M_{Ai}'$. The dashed line represents the theoretical value of $H_i = 1$ in each case.

The magnitude of random errors is also dependent on the difference between the refractive index increments of the two components since the accuracy of $Q_i$ increases as $(\nu_A - \nu_B)^2$. Thus, if the two components have similar refractive index increments, the accuracy of the technique will be considerably reduced [34-36]. For single solvents this difference is roughly equal to the difference between the two component refractive indices, and therefore independent of solvent. Mixed solvent systems have, however, been used to enhance the difference between refractive index increments for stand-alone light-scattering measurements [37, 38], and this may also be possible in a GPC/LALLS system.

It has already been shown that large differences in component calibrations are undesirable, and this consideration may affect the choice of solvent. However, copolymers such as polystyrene-polybutadiene may prove unsuitable for analysis by the GPC/LALLS technique for this reason.

Choice of concentration detectors is inextricably linked with choice of solvent. Since the refractive index increments of the two components must be different in order for the technique to work, the use of a differential refractometer as one of the concentration detectors will always be a possibility (although, of course, more suitable detectors may be found in practice). This could be used in conjunction 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 analyzer [39], crystal mass detector [40], or densimeter [41, 42]). One problem with spectroscopic detectors is finding suitable windows, and this may restrict the use of mixed solvents. Elimination of the delay between detectors is desirable, and this could be achieved by using a Fourier-transform infrared [43, 44] or rapid-scanning ultraviolet spectrometer [45] as the only concentration detector. However, this is an expensive option and still does not eliminate the delay between the LALLS detector and the concentration detector.

The above considerations show that no single solvent/detector combination suitable for most copolymer types can be found. Careful consideration of the most suitable solvent type is essential before commencing work on a new copolymer type.

## GPC/LALLS ON PS-PDMS BLOCK COPOLYMERS

As reported in Ref. 32, the copolymer GPC/LALLS technique has been tested on a series of diblock copolymers and blends of polystyrene (PS) with poly(dimethylsiloxane) (PDMS).

The chosen solvent was tetrachloroethylene. The refractive index increments for PS and PDMS in this solvent were measured as 0.0934 and -0.0932 $cm^3/g$, respectively, at 25°C. The light-scattering requirements of this solvent are therefore ideal.

This work was conducted with the assumption that $P_i$ was zero throughout. Although the use of Eq. (10) should give better results, the two component calibrations are very similar, and the errors in $H_i$ arising from this assumption should remain within 8% overall, and generally less (see Fig. 1a).

## Experimental

The PS-PDMS block copolymers were previously prepared and partially characterized by G. Taylor at Loughborough University of Technology [46, 47]. Anionic processes were used in the preparation to polymerize hexamethylcyclotrisiloxane onto polystyryllithium blocks. $\bar{M}_n$ for the polystyryllithium blocks (obtained prior to copolymerization) and $\bar{M}_w/\bar{M}_n$ for the overall copolymers were obtained by GPC, and composition by silicon analysis.

The chromatographic setup is illustrated in Fig. 3. Four PLgel 30-cm columns containing 10-$\mu$m packing were used, maintained at 80°C to ease solvent flow, and the LALLS photometer was a Model KMX-6 instrument from Chromatix. Sample concentrations were 5 $mg/cm^3$, and 0.1% toluene was used as an internal marker.

For further experimental details, see Ref. 32.

## Results and Discussion

The GPC columns were initially calibrated with narrow PS standards, all peak elution volumes being corrected to a flow rate of 1 cm/min. Values of $\bar{M}_w$ and their corresponding elution volumes were then obtained for a series of PS and PDMS samples with the LALLS detector. These experimental values were used, in conjunction with Mark-Houwink exponents obtained from viscometry, to obtain an overall calibration for each homopolymer type expressed as a correction to the original PS standard calibration. In principle the viscometry data were not necessary, but since the PDMS calibration was based on only four GPC/LALLS runs (Fig. 4), it was felt that, used according to the universal calibration method of Grubisic et al. [30], the viscometry data would provide a more accurate measurement of the relative calibration slopes.

The GPC/LALLS system was first tried out on a series of blends. The same two samples of PS and PDMS were mixed in different proportions. The results

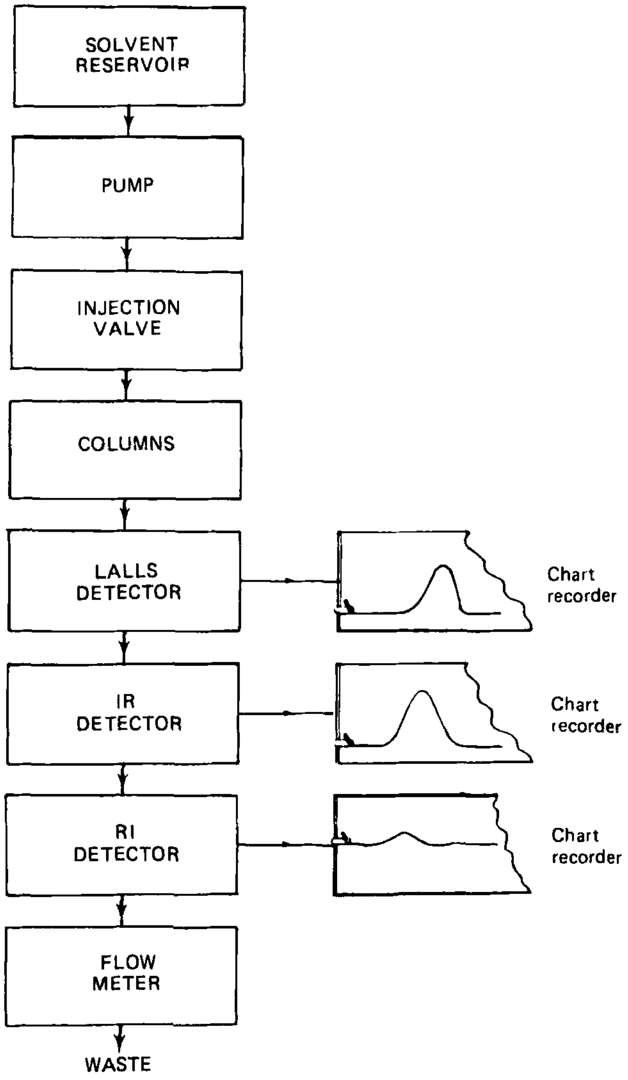

FIG. 3. GPC/LALLS setup used for analysis of PS-PDMS copolymers.

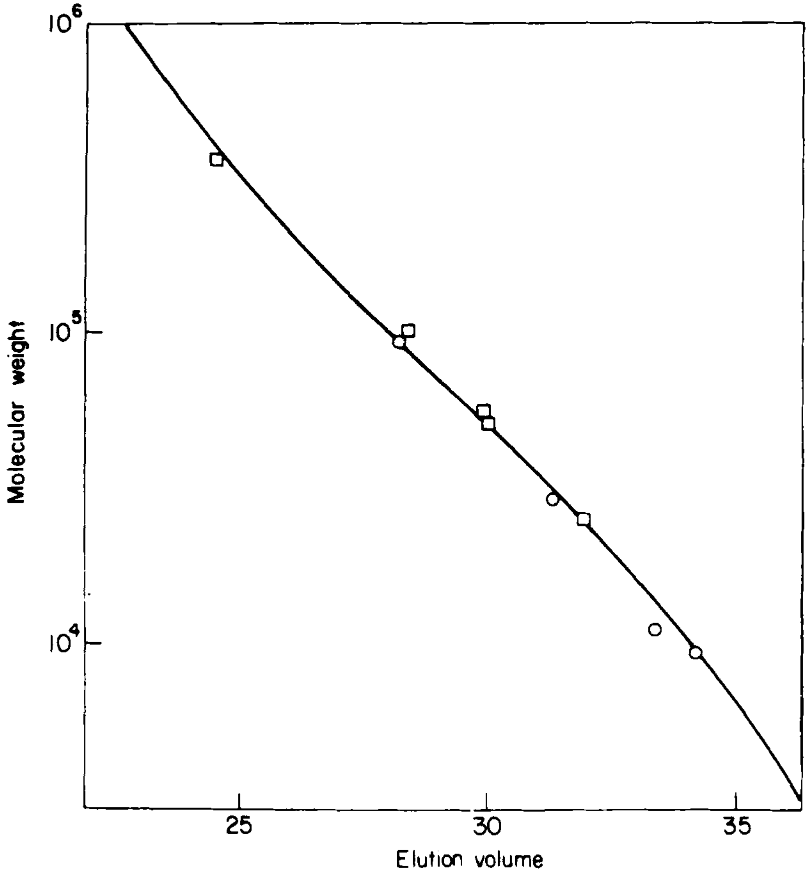

FIG. 4. Points obtained for PS (□) and PDMS (○) column calibrations by GPC/LALLS compared to an original calibration with narrow-MWD PS standards (——). Reproduced from Ref. 32 by kind permission of Butterworth & Co. (Publishers) Ltd.

were initially analyzed as blend data without reference to the LALLS trace. Thus the concentration of each component at each elution volume was calculated, and hence an MWD for each component. Values of $\bar{M}_w$ and overall composition are in good agreement except for blends with a low PS content (Table 1), when the PS MWD becomes considerably distorted. Values of $\bar{M}_n$,

TABLE 1. Analysis of Blend GPC Results with Calculated Component Molecular Weights Compared with Those of the Original Homopolymers Mixed Together

| | | | | | Homopolymer results |
|---|---|---|---|---|---|
| % PS weighed out | 20.5 | 40.2 | 59.5 | 75.9 | |
| % PS from GPC | 16.8 | 39.6 | 61.5 | 75.5 | |
| PS $\bar{M}_n$ | 5 300 | 9 100 | 11 100 | 9 600 | 11 400 |
| PS $\bar{M}_w$ | 30 800 | 44 600 | 43 000 | 43 900 | 43 600 |
| PDMS $\bar{M}_n$ | 12 700 | 13 800 | 12 700 | 14 700 | 17 100 |
| PDMS $\bar{M}_w$ | 34 400 | 35 100 | 34 600 | 35 500 | 35 800 |

however, are much worse. This is believed to be due to inconsistencies between the two concentration detectors since poor agreement was found between $\bar{M}_n$ values for single homopolymers run individually, while $\bar{M}_w$ agreement was good [32].

If each sample is treated as a copolymer of unknown heterogeneity, it is necessary to make use of the LALLS trace before the component $\bar{M}_w$ values can be found. The values thus obtained, together with the heterogeneity parameters found by using GPC/LALLS, are shown in Table 2. The $\bar{M}_w$ values are almost as good as those obtained knowing the sample to be a blend and $H$ values are in excellent agreement with the theoretical value of 1. Values of $Q$ are in fairly good agreement with theory, $P$ values (actually available without recourse to LALLS) less so, presumably because of the detector inconsistencies at low molecular weight. Despite the good overall $H$ values, individual $H_i$ values are less accurate, especially at low molecular weight or when one component dominates the composition (Fig. 5). The errors in $H_i$ are generally greater than those expected due only to effect of ignoring $P_i$.

PS-PDMS block copolymers were analyzed in a similar way, and the main results are summarized in Table 3. Where possible, the measurements of Taylor on these samples [46] are included for comparison. For all the samples, overall compositions are in good agreement.

B16, B20, and B22 give good agreement in $\bar{M}_w$ and reasonable agreement in $\bar{M}_n$. They appear to be good copolymers with consistently low hetero-

TABLE 2. Analysis of Blends as "Unknown Copolymers" by Using GPC/LALLS Results. $\bar{M}_{w\text{PS}}$ and $\bar{M}_{w\text{PDMS}}$ Values Should Be the Same as the Original Homopolymer $\bar{M}_w$'s, Which Are Also Shown for Comparison. $H$ Should Be 1 for All Blends

| | | | | | Homopolymer results |
|---|---|---|---|---|---|
| % PS weighed out | 20.5 | 40.2 | 59.5 | 75.9 | |
| $\bar{M}_{w\text{PS}}$ | 31 000 | 41 200 | 40 500 | 44 800 | 43 600 |
| $\bar{M}_{w\text{PDMS}}$ | 35 300 | 35 900 | 34 700 | 43 500 | 35 500 |
| $P$ | -900 | 1 400 | 1 200 | 900 | |
| $P$ (theory) | 1 300 | 1 900 | 1 800 | 1 400 | |
| $Q$ | 4 400 | 9 100 | 8 400 | 8 600 | |
| $Q$ (theory) | 6 800 | 9 700 | 9 400 | 6 900 | |
| $H$ | 1.02 | 0.97 | 0.96 | 1.06 | |

geneity (see, for example, Fig. 6a). The values of $P$ and $Q$ may be compared with those expected from random-coupling statistics [11]:

$$P = W(1 - W)\,[\bar{M}_{w\text{PS}} - \bar{M}_{n\text{PS}} - (\bar{M}_{w\text{PDMS}} - \bar{M}_{n\text{PDMS}})] \tag{11}$$

$$Q = W(1 - W)\,[(1 - W)(\bar{M}_{w\text{PS}} - \bar{M}_{n\text{PS}}) + W(\bar{M}_{w\text{PDMS}} - \bar{M}_{n\text{PDMS}})] \tag{12}$$

The component $\bar{M}_n$ and $\bar{M}_w$ values can all be obtained from the GPC/LALLS results. However, the $\bar{M}_n$ values are inaccurate in this case for the reasons already described. Use of the $\bar{M}_n$ values obtained by Taylor with results otherwise obtained by GPC/LALLS, however, gives excellent agreement with theory, as shown in Table 4, except for B20, which has lower accuracy because of its low molecular weight.

B12 and B13 appear to be homopolymer blends of low molecular weight PDMS with high molecular weight PS (see, for example, Fig. 6b). The disagreement with Taylor's $\bar{M}_w$ values arises because he only measured the homopolymer PS molecular weight before copolymerization, his calculation of copolymer molecular weights being dependent on no PDMS homopolymer being formed. Assuming that the samples are blends, calculation of PS

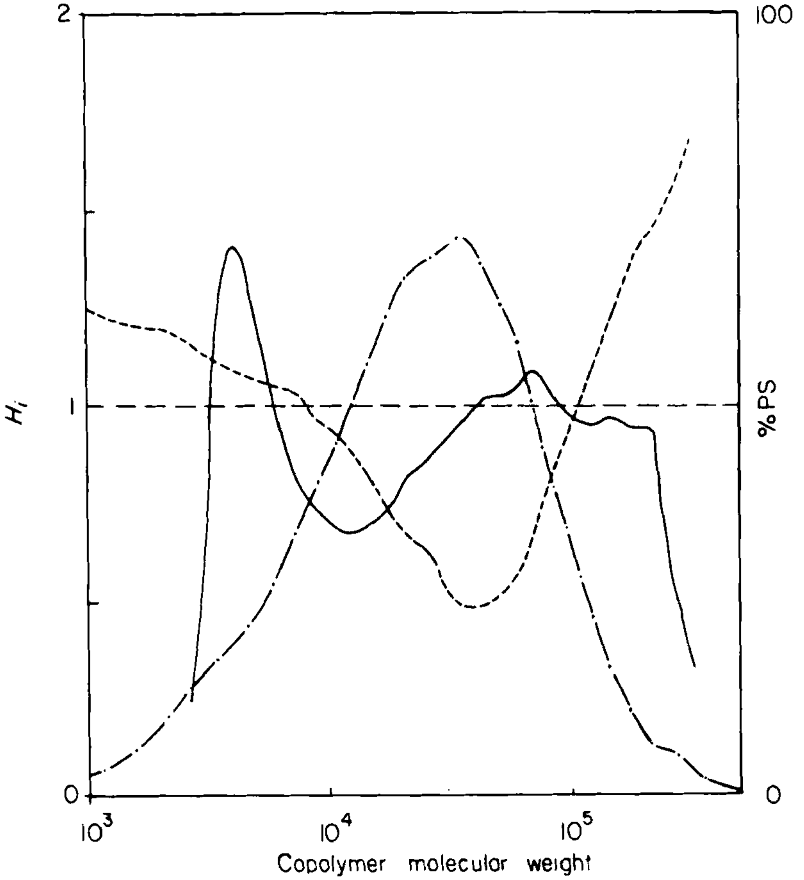

FIG. 5. Variation of the compositional heterogeneity (——) and composition (- -) with the MWD (- •) of a PS-PDMS blend containing 40.2% PS. Reproduced from Ref. 32 by kind permission of Butterworth & Co. (Publishers) Ltd.

$\bar{M}_w$'s from Taylor's results gives excellent agreement for B13 ($\bar{M}_{w\text{PS}}$ = 65 400) and reasonable agreement for B12 ($\bar{M}_{w\text{PS}}$ = 59 900) with the GPC/LALLS results. It is worth noting that Taylor rejected these two samples for the work described in Ref. 47 due to their high polydispersity.

B21 appears to be a high molecular weight copolymer with some low molecular weight homopolymer blend (Fig. 6c) although, in this case, there is no additional evidence to support or oppose this interpretation.

TABLE 3. Main Results from GPC/LALLS Analysis of PS-PDMS Copolymers[a]

| | B12 | B13 | B16 | B20 | B21 | B22 |
|---|---|---|---|---|---|---|
| % PS | 60.7 | 44.3 | 74.8 | 79.7 | 32.1 | 70.0 |
| % PS (Taylor) | 61.2 | 42.9 | 76.1 | 79.7 | 32.1 | 70.8 |
| $\bar{M}_n$ | 14 600 | 10 600 | 53 100 | 14 600 | 10 700 | 38 700 |
| $\bar{M}_n$ (Taylor) | 74 000 | 106 500 | 57 300 | 15 900 | 36 500 | 47 200 |
| $\bar{M}_{w\mathrm{PS}}$ | 65 200 | 66 100 | 54 300 | 17 200 | 14 800 | 44 200 |
| $\bar{M}_{w\mathrm{PDMS}}$ | 13 100 | 21 300 | 21 000 | 5 100 | 25 100 | 18 700 |
| $\bar{M}_w$ | 50 700 | 40 600 | 68 000 | 20 600 | 31 600 | 56 700 |
| $\bar{M}_w$ (Taylor) | 96 900 | 152 300 | 67 000 | 18 900 | 45 300 | 53 800 |
| $P$ | 11 700 | 11 000 | 800 | 200 | 0 | 1 300 |
| $Q$ | 6 600 | 11 600 | 1 400 | 300 | 1 500 | 1 300 |
| $H$ | 0.82 | 1.01 | 0.25 | 0.22 | 0.38 | 0.23 |

[a] Results obtained by Taylor on the same copolymers are included for comparison.

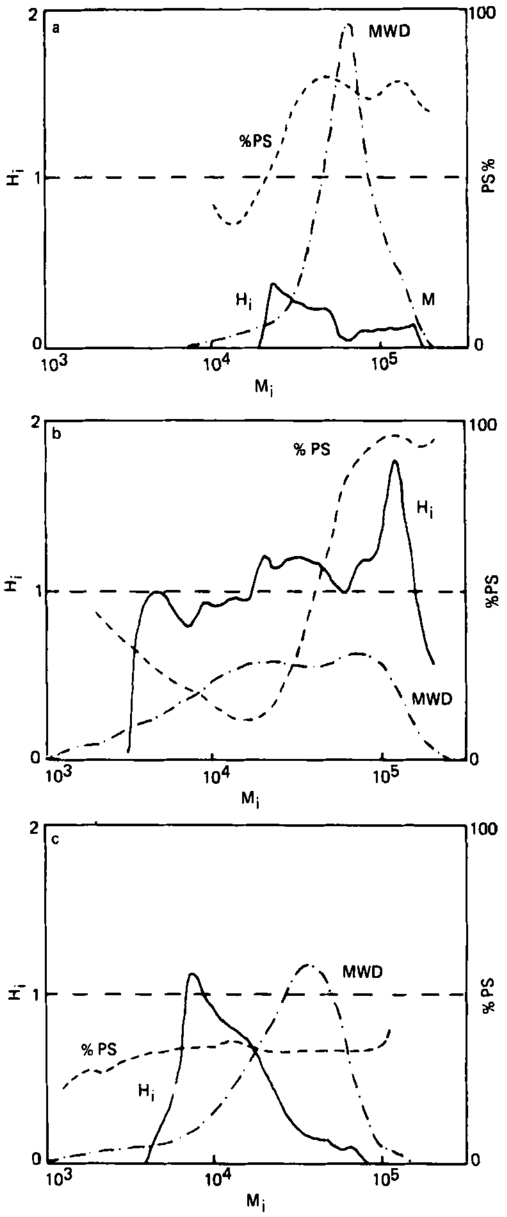

FIG. 6. Variation of the compositional heterogeneity (—) and composition (- -) with the MWD (- ·) of representative PS-PDMS copolymers: (a) B16, (b) B13, and (c) B21. Reproduced from Ref. 32 by kind permission of Butterworth & Co. (Publishers) Ltd.

TABLE 4. Comparison of GPC/LALLS $P$ and $Q$ Values with Those Expected from Block Copolymerization Equations

| | B16 | B20 | B22 |
|---|---|---|---|
| $P$(GPC/LALLS) | 800 | 200 | 1,300 |
| $P$(Eq. 11) | 800 | 400 | 1,400 |
| $Q$(GPC/LALLS) | 1,400 | 300 | 1,300 |
| $Q$(Eq. 12) | 1,400 | 400 | 1,400 |

## OVERALL EVALUATION

The PS-PDMS results have generally been in good agreement with what supporting evidence is available. Good results have been obtained down to an $\bar{M}_w$ of around 30 000, and this suggests that satisfactory results may be obtained when

$$(\nu_A - \nu_B)^2 \bar{M}_w \geqslant 1000, \tag{13}$$

provided the solvent refractive index falls between those of the two component homopolymers.

The experiments described here have tested the system with samples whose properties are well suited to this technique, i.e., block copolymers whose two components have similar molecular weight GPC calibrations and dissimilar refractive index increments. Dissimilar GPC calibrations should present serious problems only in extreme cases. Similar refractive index increments are likely to be more of a limitation on the technique, as illustrated by Eq. (13). It is not clear at present how feasible the use of mixed solvents would be in overcoming this.

The main problems encountered in the PS-PDMS experiments concern inconsistencies between the two concentration detectors, apparently a problem with the IR cell (possibly adsorption of PDMS onto the cell windows). This has caused fewer problems with copolymers than with blends and has not greatly affected overall heterogeneity parameters. It does, however, show the value of testing the GPC/LALLS system with blends and well illustrates the type of idiosyncracies encountered with multiple detector work.

It is unlikely that the GPC/LALLS technique could be successfully used on systems other than block copolymers unless the molecular weights of the eluting molecules were measured directly, e.g., using an on-line viscometer [29].

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