

# Determination of the molecular weight and compositional heterogeneity of block copolymers using combined gel permeation chromatography and low-angle laser light scattering

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A procedure, using combined gel permeation chromatography and low-angle laser light scattering, has been developed for characterizing block copolymers. A compositional heterogeneity parameter, whose variation with molecular weight can be measured, has been defined. The procedure has been applied to copolymers and blends of polystyrene and poly(dimethylsiloxane).

(Keywords: copolymer characterization; compositional heterogeneity; gel permeation chromatography; low-angle laser light scattering)

## INTRODUCTION

Gel permeation chromatography (g.p.c.) has long been established as a technique for determining the molecular weight distribution (*MWD*) of polymers. In general, however, copolymer samples have not only a *MWD* but also a simultaneous distribution of compositions. This makes the *MWD*'s of copolymers difficult to measure using g.p.c., for the molecules are separated not according to molecular weight, but according to their size in solution. The problem has been overcome in some cases by using selective detectors to establish the copolymer composition at each elution volume and some form of interpolation between the column molecular weight calibrations for the component homopolymers<sup>1</sup>.

Information on copolymer composition distributions had, in the past, been very limited unless time-consuming cross fractionation techniques were used<sup>2-4</sup>. This paper describes how the addition of a low-angle laser light scattering (LALLS) photometer onto a dual concentration detector g.p.c. system can be used to determine compositional heterogeneity at each elution volume and hence a large amount of information about the overall composition and its correlation with the *MWD* for a two component block copolymer.

## CALCULATION OF MOLECULAR WEIGHT DISTRIBUTIONS

A g.p.c. molecular weight calibration curve for a particular homopolymer may often be obtained using

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narrow *MWD* samples, having known molecular weights, of that polymer. Unfortunately, the range of calibrant polymer types available is limited and universal calibration procedures are frequently employed for conversions from one polymer type to another<sup>5</sup>. A more direct method of obtaining molecular weight calibrations for different polymer types, and one more consistent with the work described in this paper, is to use on-line LALLS for molecular weight monitoring<sup>6</sup>.

For a g.p.c./LALLS system the excess Rayleigh factor,  $R_{\theta i}$ , due to scattering from the solute alone, at the *i*-th elution volume interval may be related to the molecular weight,  $M_i$ , of the molecules eluting at that interval according to the equation:

$$\frac{K^*v^2c_i}{R_{\theta i}} = \frac{1}{M_i} + 2A_{2i}c_i \quad (1)$$

where  $c_i$  is the concentration of molecules,  $A_{2i}$  is their light scattering second virial coefficient in solution,  $v$  is the overall refractive index increment and  $K^*$  is a function of the light wavelength and solvent refractive index. If a known weight of polymer is injected,  $c_i$  can easily be calculated from the concentration detector response.  $A_{2i}$  varies only slightly with molecular weight and may be taken as the second virial coefficient for any sample of the same type or, since its contribution to the final result is only about 1%, it can be ignored altogether. From the  $M_i$  values calculated for a particular sample it should be possible, provided the sample does not have a very broad *MWD*, to construct a calibration curve which approximates to

$$\log M = aV + b \quad (2)$$

where  $M$  is the molecular weight,  $V$  is the elution volume, and  $a$  and  $b$  are constants for the calibration.

In practice the  $M_i$  values calculated near the centre of a polymer's  $MWD$  tend to be the most accurate and each calibration point can be weighted according to the size of the detector responses before applying a least squares procedure<sup>7</sup>.

An accurate value of the weight-average molecular weight ( $\bar{M}_w$ ) should be expected from g.p.c./LALLS and substitution of this value, together with the calculated values of  $a$  and  $b$ , into equation (2) will yield a corresponding elution volume which also should be accurate.

If several samples of a particular homopolymer type are run, therefore, it should be possible to obtain an accurate set of  $\bar{M}_w$  values, together with their corresponding elution volumes. These can then be used to get a full column calibration for that homopolymer type. In the case of a diblock copolymer one such calibration is required for each component homopolymer and an interpolation technique, such as that used by Runyon *et al.*<sup>1</sup>, may then be used between the two calibrations. Although other methods of interpolation are available<sup>8,9</sup>, there is very little difference in the resultant  $M_i$  values as long as the two component calibrations are not vastly different and there are no strong interactions between the copolymer blocks<sup>7,8</sup>.

## CALCULATION OF COMPOSITIONAL HETEROGENEITY

### Heterogeneity parameters $P$ , $Q$ and $H$

The parameters most frequently used to quantify the compositional heterogeneity of a copolymer sample, as measured using light scattering data, are  $P$ , representing the molecular weight influence on compositional heterogeneity, and  $Q$ , which represents the overall compositional drift. These two parameters are defined as<sup>10</sup>:

$$P = \frac{\sum_j c_j M_j (W_j - W)}{\sum_j c_j} \quad (3)$$

$$= \frac{1}{2} [(1 - W)(\bar{M}_w - \bar{M}_{wB}) - W(\bar{M}_w - \bar{M}_{wA})]$$

$$Q = \frac{\sum_j c_j M_j (W_j - W)^2}{\sum_j c_j} \quad (4)$$

$$= W(1 - W)(\bar{M}_{wA} + \bar{M}_{wB} - \bar{M}_w)$$

where  $j$  refers to all molecules of a particular molecular weight and composition,  $W$  represents the overall composition and  $\bar{M}_{wA}$  and  $\bar{M}_{wB}$  are the weight average molecular weights of the two components, A and B, in the diblock copolymer.

It may be more meaningful to use another parameter,  $H$ , defined as

$$H = Q/Q_{\max} \quad (5)$$

where  $Q_{\max}$  is the value of  $Q$  obtained for a homopolymer blend.  $H$  therefore takes a value between 0 (for a compositionally homogeneous sample) and 1 (for a homopolymer blend, i.e. maximum heterogeneity).

### The use of g.p.c./LALLS in measuring compositional heterogeneity

In a g.p.c./LALLS experiment, equation (1) should give value values for  $M_i$  as long as all the polymer molecules in the scattering beam are identical. In the case of copolymers both molecular weight and compositional heterogeneity may be expected and this leads to an increase in the excess Rayleigh factor. Equation (1) must therefore be replaced by:

$$\frac{K^* v_i^2 c_i}{R_{\theta i}} = \frac{1}{M_i^*} + 2A_2 c_i \quad (6)$$

where  $M_i^*$  is the apparent molecular weight and  $v_i$  is the refractive index increment for all components at the  $i$ -th elution volume interval. If one assumes a linear relationship between refractive index increment and composition, it is easy to calculate  $v_i$  from the homopolymer refractive index increments,  $v_A$  and  $v_B$ , and the calculated  $W_i$  value. The assumption, together with the fact that the second virial coefficient term in equation (6) can be ignored, also allows  $M_i^*$  to be expressed as<sup>10</sup>:

$$M_i^* = M_{w_i} + 2P_i \left( \frac{v_A - v_B}{v_i} \right) + Q_i \left( \frac{v_A - v_B}{v_i} \right)^2 \quad (7)$$

where  $M_{w_i}$ ,  $P_i$  and  $Q_i$  are the  $\bar{M}_w$ , and the  $P$  and  $Q$  values of the molecules eluting at the  $i$ -th elution volume interval.

If the two component homopolymer calibrations are not too different there should be a reasonably narrow range of molecular weights present at each elution volume. The  $P_i$  term in equation (7) therefore can be ignored and  $M_{w_i}$  replaced by  $M_i$ . This leads to:

$$M_i^* = M_i + Q_i \left( \frac{v_A - v_B}{v_i} \right)^2 \quad (8)$$

Enough information exists, therefore, to allow the calculation of  $Q_i$ .  $H_i$ , the value  $H$  at the  $i$ -th elution volume interval, can be calculated by assuming a maximum  $Q_i$  value of

$$Q_{i,\max} = W_i(1 - W_i)[(1 - W_i)M_{A_i} + W_i M_{B_i}] \quad (9)$$

Clearly,  $H_i$  may vary from 0 to 1 in the same way as  $H$ .

A narrow  $MWD$  at each elution volume has been assumed, so both the weight and number average molecular weight at the  $i$ th elution volume interval should be equal to  $M_i$ . Consequently, the values for the individual components may be calculated as:

$$\bar{M}_{w,iA} = W_i M_i + Q_i / W_i \quad (10)$$

$$\bar{M}_{n,iA} = W_i M_i \quad (11)$$

$$\bar{M}_{w,iB} = (1 - W_i) M_i + Q_i / (1 - W_i) \quad (12)$$

$$\bar{M}_{n,iB} = (1 - W_i) M_i \quad (13)$$

These can be averaged in the appropriate manner to obtain molecular weight values for the overall sample and the individual components. Such values then may be used in calculating the overall heterogeneity parameters from equations (3), (4) and (5).

## EXPERIMENTAL

A Chromatix KMX-6 LALLS photometer was used for both 'static' or ('stand-alone') light scattering measurements and as an on-line g.p.c. detector. Refractive index increments were determined using a Chromatix KMX-16 laser differential refractometer.

The g.p.c. components were, in sequence, a pump (Du Pont Instruments, model 870), an injection valve (Spectroscopic Accessories, model 3.100, fitted with a 0.25 cm<sup>3</sup> loop), an in-line depth filter (Rheodyne, 2 μm), four 30 cm columns with 10 μm packings (Polymer Laboratories Ltd.; quoted pore sizes 10<sup>3</sup> Å, 10<sup>4</sup> Å, 10<sup>5</sup> Å and 10<sup>6</sup> Å), another depth filter, a 0.2 μm PTFE membrane filter (Millipore), the LALLS photometer fitted with a low volume flow-through cell, an infra-red detector (Wilks-Miran model 1A), a refractive index detector (Waters Associates, model R401) and a liquid flow-meter (Phase Separations Ltd.). The g.p.c. solvent was tetrachloroethylene (redistilled) and solution concentrations of 5 × 10<sup>-3</sup> g cm<sup>-3</sup>, or less, were used; 0.1% of toluene was added as an internal marker.

Solution viscometry measurements were performed using an Ubbelohde viscometer at 25°C.

All samples of the diblock copolymer polystyrene-poly(dimethylsiloxane) (abbreviated to PS-PDMS) were prepared by anionic polymerization techniques by the addition of hexamethylcyclotrisiloxane to 'living' poly(styryllithium). Complete synthetic details are given elsewhere<sup>11</sup>. PS-PDMS samples B16, B20, B21 and B22 were reported in an earlier paper<sup>12</sup> and were presumed to have narrow distributions in molecular weight and composition. PS-PDMS samples B12 and B13 were more polydisperse<sup>11</sup>, and consequently had been rejected for use in the work described in ref. 12. PS-PDMS samples were characterized by g.p.c. and silicon determination, as described elsewhere<sup>12</sup>. These techniques yielded the copolymer composition (% polystyrene), the number-average molecular weight of the polystyrene block  $M_{nPS}$  (obtained by g.p.c. on deactivated poly(styryllithium), before copolymerization), the PDMS block  $M_{nPDMS}$ , and the overall copolymer  $M_n$  (both calculated from  $M_{nPS}$  and the copolymer composition, assuming a diblock structure), and the weight-average molecular weight  $M_w$  of the copolymer (calculated from  $M_n$  and the copolymer polydispersity)<sup>11</sup>.

The narrow *MWD* polystyrenes were commercially available calibrants (Polymer Laboratories Ltd.). All other homopolymers were samples submitted to the Polymer Supply and Characterization Centre for molecular weight characterization.

## RESULTS AND DISCUSSION

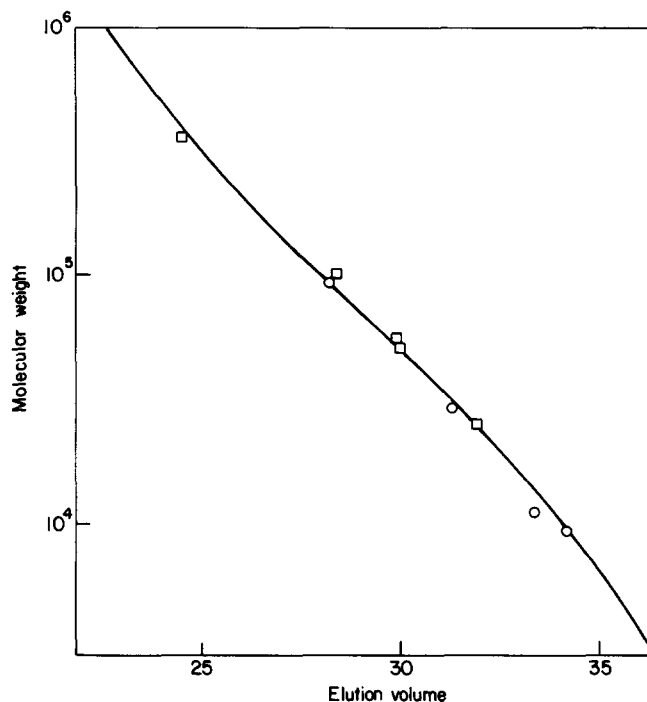
The g.p.c. system was initially calibrated using narrow *MWD* polystyrene standards. All peak elution volumes were measured from the refractive index (*RI*) detector trace and were corrected to a flow-rate of 1 cm<sup>3</sup> min<sup>-1</sup>. G.p.c./LALLS experiments were then performed on a series of polystyrene (PS) and poly(dimethylsiloxane) (PDMS) samples. An  $M_w$  value and its corresponding elution volume (corrected to 1 cm<sup>3</sup> min<sup>-1</sup>) were calculated for each sample. Values of 0.0934 cm<sup>3</sup> g<sup>-1</sup> for PS and -0.0932 cm<sup>3</sup> g<sup>-1</sup> for PDMS, as measured at 25°C, were used for the refractive index increment  $\nu$  in the calculations. Since the variation in  $\nu$  with molecular

weight was less than 2% for the range covered<sup>7</sup>, this was ignored. The results are shown in *Figure 1* and it can be seen that there is good agreement, for PS, between the two methods of calibration. Also it is clear that the calibration for PDMS is similar to that for PS.

A convenient way of relating the calibrations of the component homopolymers is in terms of the Mark-Houwink parameters which can be used to 'correct' the original calibration using the universal calibration procedure proposed by Grubisic, Rempp and Benoit<sup>5</sup>. Unfortunately, there are insufficient data in *Figure 1* alone to give an accurate correction to the curve slope, which corresponds to the Mark-Houwink exponent *a*. The actual exponent *a* values used in this work were obtained from solution viscometry measurements. The values used for the Mark-Houwink *K* parameter were those obtained from the average offset of the g.p.c./LALLS calibration points from the original calibration after slope correction. The resultant *K* and *a* values are shown in *Table 1*.

A comparison of the g.p.c. results obtained with both concentration detectors for the three PDMS samples (see *Table 2*) shows rather poor agreement in  $\bar{M}_n$  and this must be borne in mind during later interpretation.

The response of the two concentration detectors was calibrated with a series of homopolymer solutions of various concentrations and a series of prepared blends were run on the g.p.c./LALLS system. The results are summarized in *Table 3*. 'Theoretical' values for the various parameters are also shown, and these are derived from



**Figure 1** Points obtained for a column calibration using g.p.c./LALLS, as compared to an original calibration using narrow *MWD* PS standards: (—), original calibration; (□), polystyrene; (○), poly(dimethylsiloxane)

**Table 1** Mark-Houwink *K* (in cm<sup>3</sup> g<sup>-1</sup>) and *a* values used in g.p.c. work

Polymer type	<i>K</i> × 10 <sup>3</sup>	<i>a</i>
Column calibration standards	6.5	0.75
PS	6.4	0.75
PDMS	2.9	0.84

**Table 2** A comparison of the results obtained from each of the g.p.c. concentration detectors for three different PDMS samples

Sample	RI detector			I.r. detector		
	$\bar{M}_n$	$\bar{M}_w$	$\bar{M}_z$	$\bar{M}_n$	$\bar{M}_w$	$\bar{M}_z$
1	16 800	35 000	55 700	12 400	32 200	54 900
2	25 500	73 500	124 500	19 800	69 500	122 700
3	40 900	143 900	239 900	23 700	133 700	231 600

**Table 3** Overall parameters obtained from dual concentration detector g.p.c. and dual concentration detector g.p.c./LALLS for a series of blends

		Blend 1		Blend 2		Blend 3		Blend 4	
		Expt.	Theory	Expt.	Theory	Expt.	Theory	Expt.	Theory
Dual concentration detector results (results not requiring LALLS)	% PS	16.8	20.5	39.6	40.2	61.5	59.5	75.5	75.9
	$\bar{M}_{nPS}$	1 700	3 200	4 500	5 700	7 200	7 800	7 900	9 400
	$\bar{M}_{nPDMS}$	8 600	12 300	6 900	8 500	4 500	5 300	2 600	3 000
	$\bar{M}_n$	10 300	15 500	11 400	14 200	11 700	13 200	10 500	12 400
	$\bar{M}_w$	33 900	37 400	39 000	38 900	39 900	40 400	41 900	41 700
	$P$	-900	1 300	1 400	1 900	1 200	1 800	900	1 400
Additional results obtainable from knowing each sample is a blend	PS $\bar{M}_n$	5 300	11 400	9 100	11 400	11 100	11 400	9 600	11 400
	PS $\bar{M}_w (= \bar{M}_{wPS})$	30 800	43 600	44 600	43 600	43 000	43 600	43 900	43 600
	PDMS $\bar{M}_n$	12 700	17 100	13 800	17 100	12 700	17 100	14 700	17 100
	PDMS $\bar{M}_w (= \bar{M}_{wPDMS})$	34 400	35 800	35 100	35 800	34 600	35 800	35 500	35 800
G.p.c./LALLS results (not assuming the samples are blends)	$\bar{M}_{wPS}$	31 000	43 600	41 200	43 600	40 500	43 600	44 800	43 600
	$\bar{M}_{wPDMS}$	35 300	35 800	35 900	35 800	34 700	35 800	43 500	35 800
	$Q$	4 400	6 800	9 100	9 700	8 400	9 400	8 600	6 900
	$H$	1.02	1.00	0.97	1.00	0.96	1.00	1.06	1.00

homopolymer g.p.c. results and the blend composition weighed out.

The upper set of results makes use only of the dual concentration detector capability (and not the LALLS). The various  $\bar{M}_n$  values ( $\bar{M}_{nPS}$  and  $\bar{M}_{nPDMS}$  refer to the component  $\bar{M}_n$  value when considering the sample as a copolymer) show rather poor agreement with theory, but the composition and overall  $\bar{M}_w$  values are in excellent agreement in all cases except for blend 1.

The middle set of results in Table 3 show the additional information gained from the g.p.c. results by knowing that each sample is a blend. Thus an  $MWD$  can be calculated for each component; these are shown in Figure 2. The results for the PDMS  $MWD$ 's are highly consistent, but the PS results become significantly distorted at low PS content.

For the lower set of results in Table 3 no initial assumptions were made about the compositional heterogeneity of the samples (i.e. they were not assumed to be blends). The additional information was obtained by making use of the LALLS traces.

The observed inconsistencies in the various  $\bar{M}_n$  values are probably due to the problem of different detector response at low molecular weight. There are also inconsistencies for some parameters when the component they refer to is present at only low concentration (e.g.  $\bar{M}_{wPDMS}$  for blend 4).

For comparison, separate 'static' LALLS measurements were made for a prepared blend using tetrachloroethylene, toluene and tetrahydrofuran as the solvents. The measurements were analysed using the method of Bushuk and Benoit<sup>10</sup> and the results are shown in Table 4. They are generally not as good as those

obtained from g.p.c./LALLS although it is possible that better 'static' LALLS results could have been obtained with a different selection of solvents. Also, 'static' LALLS is more time consuming and yields less information.

Despite the good overall results from g.p.c./LALLS, the  $H_i$  values deviate quite significantly from their theoretical value of 1 (Figure 3). Inaccuracies are generally greatest at low molecular weight or where one component dominates the composition, and this must be borne in mind when interpreting  $H_i$  curves.

The series of PS-PDMS diblock copolymers synthesized by Taylor<sup>11,12</sup> were run on the dual concentration detector g.p.c./LALLS system in the same way as the blends and the results are summarized in Table 5. All the parameters (except  $P$ ) which could be obtained without making use of a LALLS detector were also measured by Taylor<sup>11</sup> and these are included in Table 5. All the compositions are in good agreement with those of Taylor; agreement on other parameters, however, varies from sample to sample.

For samples B16, B20 and B22, the agreement in  $\bar{M}_w$  between the dual concentration detector results and Taylor's results (see Table 5) is good. The discrepancies in the various  $\bar{M}_n$  values are probably due to the dual concentration detector inconsistencies already described, Taylor's results being superior. These samples show the lowest values of  $P$ ,  $Q$  and  $H$ , and it seems that they are probably the best three copolymers. Figure 4(a) shows an example of the type of plot obtained for these three samples showing low  $H_i$  values throughout.

To test the quality of the g.p.c./LALLS results, it is possible to compare the  $P$  and  $Q$  values obtained experimentally with those calculated for random coupling

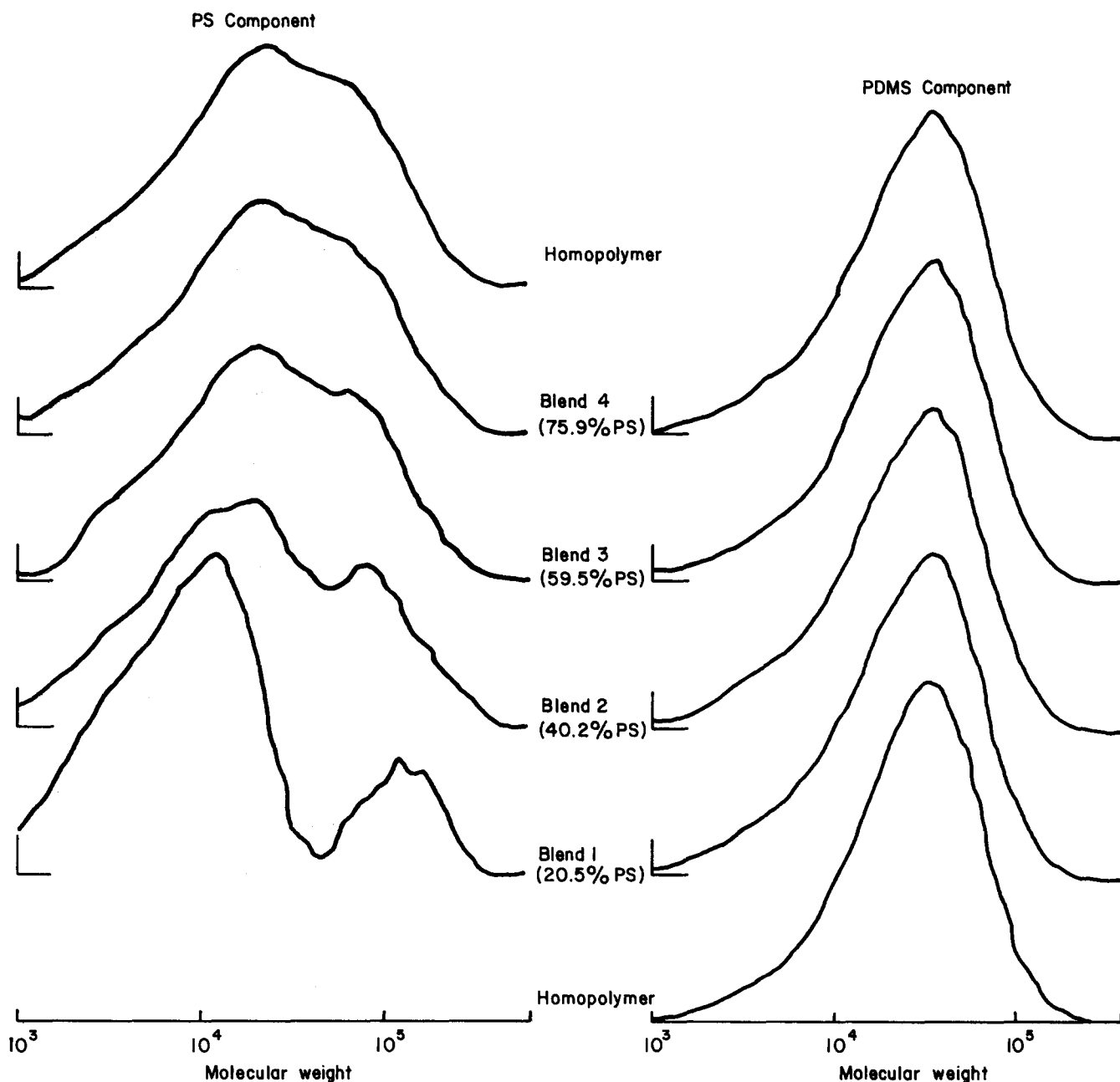


Figure 2 MWD's of blend components as calculated using dual concentration detector g.p.c.

statistics<sup>13</sup>:

$$P = W(1 - W)[\bar{M}_{wPS} - \bar{M}_{nPS} - (\bar{M}_{wPDMS} - \bar{M}_{nPDMS})] \quad (14)$$

$$Q = W(1 - W)[(1 - W)(\bar{M}_{wPS} - \bar{M}_{nPS}) + W(\bar{M}_{wPDMS} - \bar{M}_{nPDMS})] \quad (15)$$

$P$  and  $Q$  therefore have been calculated using these equations and compared with the measured values (i.e. using equations (3) and (4)). If all the parameters used in equations (14) and (15) are taken directly from g.p.c./LALLS, the  $P$  and  $Q$  values do not agree very well (Table 6, columns 1). If, however, the more accurate  $\bar{M}_{nPS}$  and  $\bar{M}_{nPDMS}$  values obtained by Taylor are substituted into the equations, very good agreement is reached (Table 6, columns 2) except in the case of B20, which is giving somewhat inaccurate results because of its low molecular weight. These results suggest that, subject to sample limitations, the g.p.c./LALLS method is correctly

Table 4 Overall parameters obtained for a PS-PDMS blend (37.5% PS) using static LALLS together with their theoretical values

Parameter	Static LALLS	Theory
$P$	13 700	8 600
$Q$	14 000	14 400
$\bar{M}_w$	28 300	52 300
$\bar{M}_{wPS}$	75 300	75 400
$\bar{M}_{wPDMS}$	12 800	38 500
$H$	1.15	1.00

measuring heterogeneity parameters and that B16, B22 and probably B20 are all good block copolymers.

There is poor agreement between this work and Taylor's results in the case of B12 and B13, the disagreement extending to  $\bar{M}_w$  as well as the various  $\bar{M}_n$  values (see Table 5). However, if any PDMS homopolymer were formed either during copolymeri-

zation or subsequently, owing to degradation, then Taylor's assumptions used in calculating molecular weights would not be valid. The g.p.c./LALLS results for sample B13 (Figure 4(b)) indicate that this sample is a blend of high

molecular weight PS and lower molecular weight PDMS. It is interesting to note that if a blend interpretation is applied to Taylor's results, a value of 65 400 is obtained for  $\bar{M}_{wPS}$ , which is in good agreement with this work. A similar picture is observed for sample B12, although the disagreement in  $\bar{M}_w$  is not as great and the g.p.c./LALLS results indicate that some copolymer is present.

Sample B21 does not show the variation in composition with molecular weight observed for B12 and B13 (Figure 4(c)), although there is generally poor agreement with the results of Taylor (see Table 5). The g.p.c./LALLS results suggest that PDMS homopolymer is again present, the sample consisting of a low molecular weight blend together with a high molecular weight copolymer. The low PS content of the sample, however, indicates that a very accurate interpretation should not be expected (c.f. blend results, Figure 2 and Table 3).

### CONCLUSION

The overall results from the combined dual concentration detector g.p.c. system with LALLS have, generally, been in very good agreement with the supporting evidence available. The plots showing the variation of heterogeneity parameter  $H_i$  and composition over the MWD range have yielded a considerable amount of additional information.

The discrepancy in the detector responses at low molecular weight does not appear significantly to affect overall heterogeneity parameters unless one of the components is overwhelmed by the other.

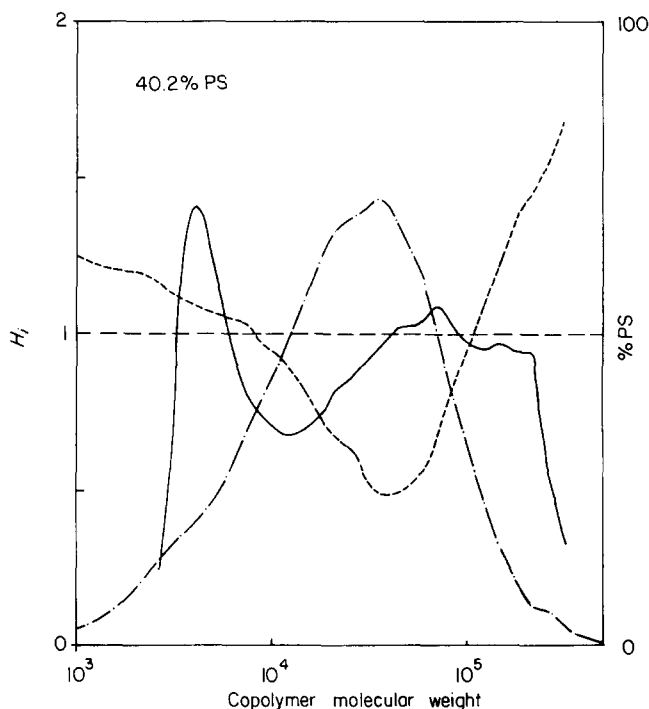


Figure 3 Variation of the compositional heterogeneity (—) and composition (---) with the MWD (-·-·-) of blend 2

Table 5 Overall PS-PDMS copolymer parameters obtained using dual concentration detector g.p.c., and the additional parameters obtained when a LALLS detector is added to the system. For comparison, the results obtained by Taylor<sup>11</sup> and, for copolymer B21, the results obtained by static LALLS are also shown

	B12		B13		B16		B20		B21			B22	
	This work	Taylor	This work	Taylor	This work	Taylor	This work	Taylor	This work	Taylor	'Static' LALLS	This work	Taylor
Dual concentration detector results													
% PS	60.7	61.2	44.3	42.9	74.8	76.1	79.7	79.7	32.1	34.8		70.0	70.8
$\bar{M}_{nPS}$	8900	45700	4700	45700	39700	43600	11700	12700	11700	12700		27100	33400
$\bar{M}_{nPDMS}$	5800	28500	5900	60800	13400	13700	2900	3200	7200	23800		11600	13800
$\bar{M}_n$	14600	74000	10600	106500	53100	57300	14600	15900	10700	36500		38700	47202
$\bar{M}_w$	50700	96900	40600	152300	68000	67000	20600	18900	31600	45300	29900	56700	53800
$P$	11700		11000		800		200		0		1600	1300	
Additional results from g.p.c./LALLS													
$\bar{M}_{wPS}$	65200		66100		54300		17200		14800		19200	44200	
$\bar{M}_{wPDMS}$	13100		21300		21000		5100		25100		20400	18700	
$Q$	6600		11600		1400		300		1500		2100	1300	
$H$	0.82		1.01		0.25		0.22		0.38		0.49	0.23	

Table 6 Theoretical  $P$  and  $Q$  values obtained using block copolymerization equations as compared with the values obtained directly from g.p.c./LALLS. Columns 1 show the theoretical results obtained using g.p.c./LALLS  $\bar{M}_{nPS}$  and  $\bar{M}_{nPDMS}$  values, and columns 2 show the results using Taylor's<sup>11</sup>  $\bar{M}_{nPS}$  and  $\bar{M}_{nPDMS}$  values.  $W$ ,  $M_{wA}$  and  $M_{wB}$  values used in the calculations were obtained from g.p.c./LALLS

Copolymer	P			Q		
	Theory (equation (14))		Directly from g.p.c./LALLS (equation (3))	Theory (equation (15))		Directly from g.p.c./LALLS (equation (4))
	1	2		1	2	
B16	1300	800	800	1800	1400	1400
B20	600	400	200	500	400	300
B22	2100	1400	1300	2200	1400	1300

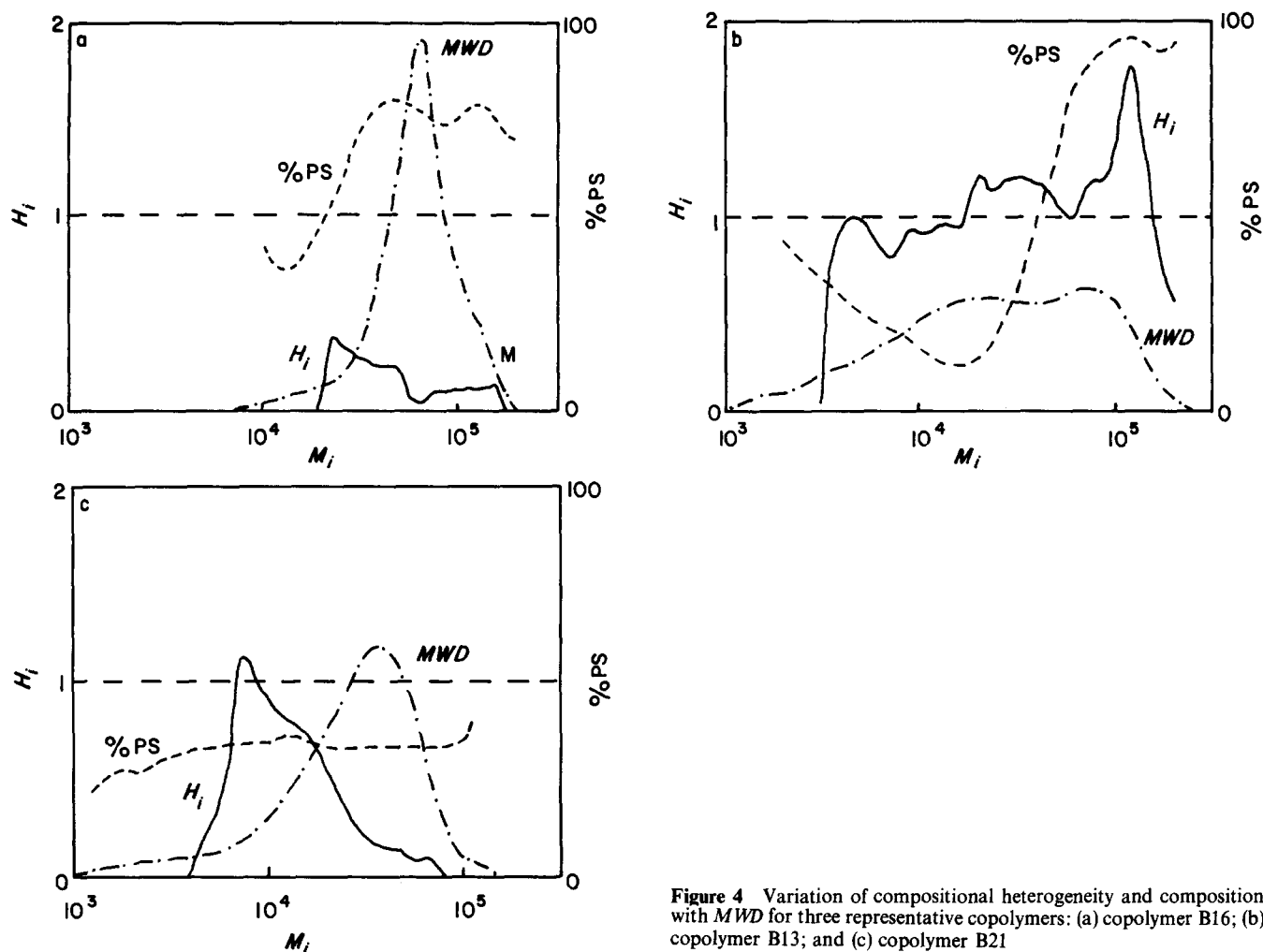


Figure 4 Variation of compositional heterogeneity and composition with *MWD* for three representative copolymers: (a) copolymer B16; (b) copolymer B13; and (c) copolymer B21

Taylor's selection of good diblock copolymers from those prepared is supported by this work.

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#### REFERENCES

- 1 Runyon, J. R., Barnes, D. E., Rudd, J. F. and Tung, L. H. *J. Appl. Polym. Sci.* 1969, **13**, 2359
- 2 Tanaka, T., Omoto, M., Donkai, N. and Inagaki, H. *J. Macromol. Sci., Phys.* 1980, **B17**, 211
- 3 Teramachi, S., Hasegawa, A. and Yoshida, S. *Macromolecules* 1983, **16**, 542
- 4 Balke, S. T. and Patel, R. D. *Adv. Chem. Sci. (Polym. Charact.)* 1983, **203**, 281
- 5 Grubisic, Z., Rempp, P. and Benoit, H. *J. Polym. Sci., B* 1967, **5**, 753
- 6 Ouano, A. C. and Kaye, W. *J. Polym. Sci., Polym. Chem. Edn.* 1974, **12**, 1151
- 7 Dumelow, T. *Ph.D. Thesis*, Loughborough University of Technology (1984)
- 8 Chang, F. S. C. *J. Chromatogr.* 1971, **55**, 67
- 9 Goldwasser, J. M. and Rudin, A. *J. Liq. Chromatogr.* 1983, **6**, 2433
- 10 Bushuk, M. and Benoit, H. *Can. J. Chem.* 1958, **36**, 1616
- 11 Taylor, G. *Ph.D. Thesis*, Loughborough University of Technology (1977)
- 12 Dawkins, J. V. and Taylor, G. *Polymer* 1979, **20**, 559
- 13 Leng, M. and Benoit, H. *J. Polym. Sci.* 1962, **57**, 263