Block Copolymer Molecular Weight by GPC

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Synopsis

Molecular weights of narrow distribution styrene–butadiene block copolymers were determined from combined GPC–intrinsic viscosity data using the universal calibration principle and from GPC data alone using the assumption of weighted average of log molecular weights suggested by Runyon et al. The results indicate that, experimentally for block copolymers in good GPC solvents, the simpler second method is more precise despite the objection on theoretical grounds raised by Ho-Duc and Prud'homme. The calibration curves of polystyrene and polybutadiene in THF were found to be parallel, and the ratio for the two molecular weights at equal elution volume was found to be 1.75, differing from the 2.0 value reported earlier.

INTRODUCTION

Runyon et al.[1] reported a method of determining composition distribution and molecular weight distribution of copolymers by GPC using an instrument equipped with two detectors. Derivation of the composition from the detector outputs was straightforward. The molecular weights of the copolymer however were assumed to be the weighted averages of the log molecular weights of the homopolymers of the constituent comonomers having the same retention volume. Thus, for a copolymer composed of monomers A and B,

$$\log M_c = x_A \log M_A + (1 - x_A)\log M_B \tag{1}$$

where M_c is the molecular weight of the copolymer, M_A is the molecular weight of homopolymer A having the same GPC retention volume, M_B is the molecular weight of homopolymer B having the same GPC retention volume, and x_A is the weight fraction of monomer A in the copolymer.

Ho-Duc and Prud'homme[2] pointed out later that this assumption implied an absence of interaction between unlike segments of the copolymer which was in conflict with their observation that there were a small number of heterocontacts. They contended therefore that the copolymer molecular weights should be computed from combined GPC–intrinsic viscosity data using the universal calibration principle.[3] Dondos, Rempp, and Benoit[4] however reported that the heterocontact effect shown in GPC measurements, while large for random copolymers of styrene and methyl methacrylate, was negligibly small for block copolymers of the same pair of monomers. Except for narrow distribution samples the combined GPC–intrinsic method requires an on-line viscometer attached to the GPC instrument.[5] Although modern automatic viscometers are more accurate, in on-line application they are still far less precise that either differential refractometer or ultraviolet absorption detectors. Thus, it is not certain that the universal calibration method will necessarily bring about better results. The purpose of this work is to examine carefully these two methods of copolymer molecular weight determinations.

EXPERIMENTAL

Polymerization

Anionic polymerizations were carried out in nitrogen-purged glass reactors. Benzene was the solvent. The initiator for preparing homopolymers and diblock copolymers of styrene and butadiene was *n*-butyllithium. The initiator for preparing styrene–butadiene–styrene triblock copolymers was a difunctional organolithium compound based the addition product of *sec*-butyllithium and bis[4-(1-phenylethenyl)phenyl] ether.[6]

Intrinsic Viscosity

A Hewlett–Packard Model 5901B autoviscometer was used for the intrinsic viscosity measurements. Uninhibited tetrahydrofuran (THF) from Burdick and Jackson Laboratories was used without further purification (same solvent as was used in GPC measurements). To avoid excess solvent evaporation, dilutions were not made in the viscometer. A fresh solution was used for each concentration.

Gel Permeation Chromatography

The GPC instrument was identical to that used by Runyon et al.,[1] except that the columns were replaced by four new Styragel columns (4-ft length) of higher efficiencies. The porosities of the column set can be described by the polystyrene calibration curve shown in Figure 1. In Figure 2 the zone-spreading parameter h, the plates per foot P, and an efficiency factor designated by P divided by the slope of the polystyrene molecular weight calibration curve were plotted. The zone-spreading parameter h as a function of elution volume was determined by a method described by Tung and Runyon.[7] The number of plates per foot P was calculated from h by the equation[8]

$$P = 2h^2V^2/L \qquad (2)$$

where V is the elution volume and L is the total column length which for the present column set is 16 ft. As shown in Figure 2, the plate count for low molecular weight material is close to 3000 plates per foot, but for molecular weights between 50,000 and 500,000 the plate count was between 300 and 600 plates per foot. The efficiency factor $P/(d \log M/dV)$ is the plate count divided by the slope of the polystyrene calibration curve shown in Figure 1. It has the same significance as the resolution for chromatographic columns used by Yau et al.[9] A sharp decrease of efficiency with molecular weight is also shown in Figure 2. This behavior is typical in GPC.

RESULTS AND DISCUSSION

Universal Calibration

Hydrodynamic volume represented by the product of molecular weight and intrinsic viscosity has been used as a universal parameter for GPC calibration.[3] Thus, if the primary calibration standards are polystyrene, then at equal elution volume:
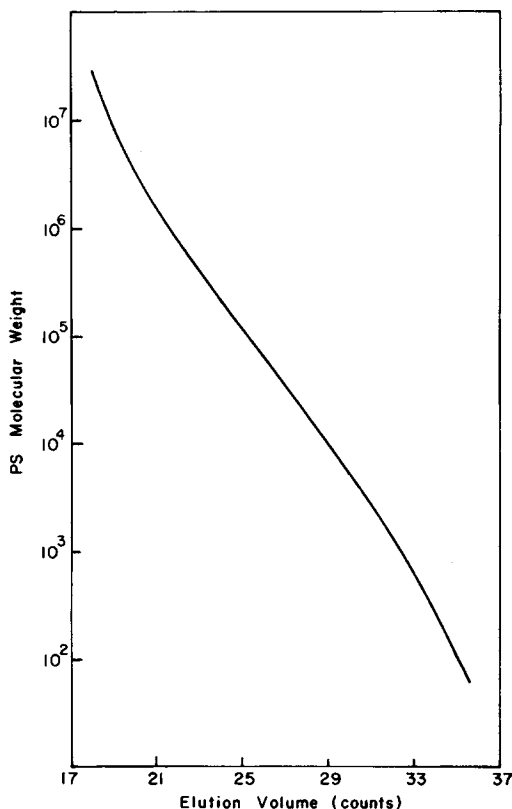
Fig. 1. Molecular weight calibration.

$$M[\eta] = M_{PS}[\eta]_{PS} \tag{3}$$

where M and $[\eta]$ are the molecular weight and the intrinsic viscosity of the unknown polymer and M_{PS} and $[\eta]_{PS}$ are the corresponding variables for polystyrene. If the Mark–Houwink constants K and α in eq. (4),

$$[\eta] = KM^{\alpha} \tag{4}$$

for both polymers are known, the calibration for polystyrene is readily convertible to that for the unknown polymer. Usually, however, the intrinsic viscosity for the unknown must be experimentally determined. Even for polystyrene in THF the values for K and α reported in the literature[8] are widely divergent with K ranging from 0.68×10^{-4} to 1.6×10^{-4} and α ranging from 0.706 to 0.766. Five narrow distribution polystyrene standards obtained from the Pressure Chemical Company were therefore used to redetermine K and α. The weight-average molecular weights which were reported[10] previously for these samples are shown in Table I. The intrinsic viscosities were determined in THF at 25°C. The data set in Table I were plotted also in Figure 3, and the straight line passing through the experimental points represents 1.119×10^{-4} for K and 0.725 for α. These values agreed closely with those reported by Goedhart and Opschoor[11] and were used in the calculations of this work.
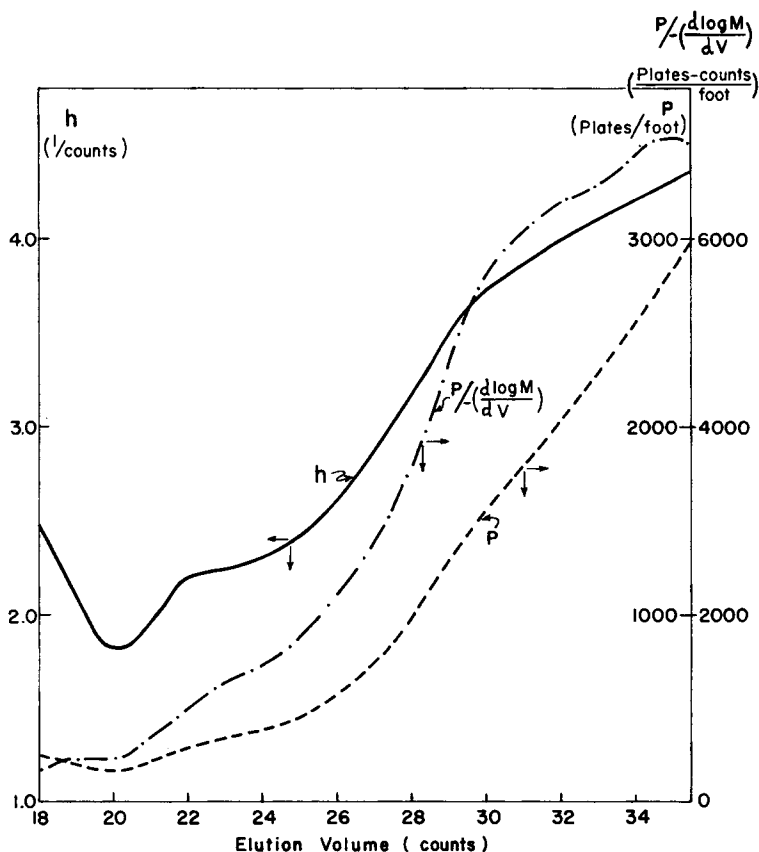
Fig. 2. Zone spreading, plate counts, and column efficiency.

TABLE I
Intrinsic Viscosities and Weight Average Molecular Weights of Standard Polystyrene Samples

Sample no.	$[\eta]$, dl/g	M_w
6a	2.25	829,000
3a	1.32	405,000
1a	0.646	159,000
4a	0.464	97,200
7a	0.293	50,600

Polybutadiene Molecular Weight Calibration

Runyon et al.[1] reported that polystyrene and polybutadiene calibration curves were parallel and that the ratio of the molecular weights of the two polymers at equal elution volume was 2.0. The polybutadiene samples used by them were obtained from Phillips Petroleum Company. The characteristics of these samples determined in the Phillips laboratories are listed in Table II.

In the calibration of Runyon et al., the weight-average molecular weights in Table II were used to correlate with the peak elution volumes. Since a ±10% error was possible in these molecular weight determinations, a further examination of the polybutadiene calibration is warranted. The new polybutadiene calibration used four of the five Phillips samples and four new polybutadiene

TABLE II
Characteristics of Phillips Polybutadiene Samples

	Microstructure[a]				
Sample	1,2	Trans	Cis	M_w[b]	M_n[c]
PE 503-D4338	7.4	49.1	43.5	$1.70 \pm 0.17 \times 10^4$	$1.61 \pm 0.16 \times 10^4$
PE 604-D4562	8.4	44.5	47.1	$1.70 \pm 0.17 \times 10^5$	$1.35 \pm 0.13 \times 10^5$
PE 503-D4336	6.7	43.5	49.8	$2.72 \pm 0.27 \times 10^5$	$2.06 \pm 0.20 \times 10^5$
PE 503-D4335	7.7	43.6	48.7	$3.32 \pm 0.33 \times 10^5$	$2.26 \pm 0.22 \times 10^5$
PE 503-D4339	6.6	41.7	51.7	$4.23 \pm 0.42 \times 10^5$	$2.86 \pm 0.28 \times 10^5$

[a] By IR.
[b] By light scattering in n-heptane at 35°C.
[c] By osmometry in toluene at 37°C.

samples prepared in our own laboratory. The results are listed in Table III and also plotted in Figure 3.

In Table III the weight-average molecular weights shown in column 3 were calculated from the polybutadiene chromatograms using polystyrene calibration. Zone spreading effect had been corrected. These molecular weights were then used as M_{PS} in the universal calibration relation eq. (3) in calculating the polybutadiene molecular weights listed in column 5. The intrinsic viscosities listed in column 4 and $[\eta]_{PS}$ calculated from M_{PS} using the Mark–Houwink relation were used in the same calculation. In Figure 3 the line correlating the intrinsic viscosities of polybutadiene and their molecular weights is shown to be parallel to the line for polystyrene. It follows from the universal calibration relation that the GPC calibration curves for the two polymers are also parallel, confirming the observation by Runyon et al.[1] The average ratio of the two molecular weights at equal elution volume is 1.75 as shown in Table III, differing from the 2.0 value reported earlier.

If the molecular weights corresponding to the peak of the chromatograms had been used in the universal calibration calculations the ratio of the two molecular weights would turn out to be 1.70. Since whole samples were used in intrinsic viscosity measurements, the use of the weight-average molecular weights for M_{PS} is more appropriate.

The M_w and M_n calculated from the chromatograms of the four Phillips polybutadiene samples using the average ratio of 1.75 are shown in Table IV.

TABLE III
GPC and Intrinsic Viscosity Results on Polybutadiene Samples

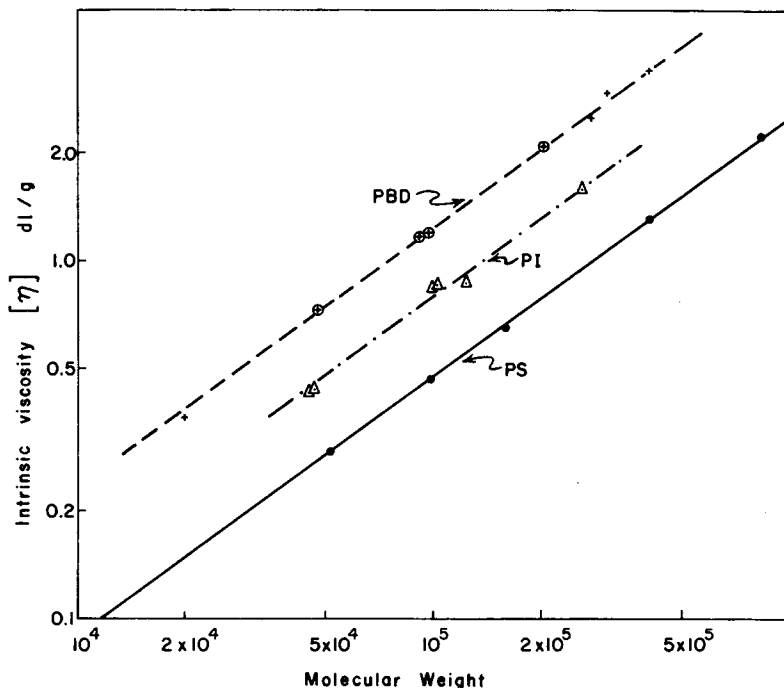|	GPC				
Sample	Peak count	$M_w \times 10^{-3}$ PS scale	$[\eta]$, dl/g	PBD $M_w \times 10^{-3}$, by eq. (3)	M_{PS}/M_{PBD}
PE 503-D4338	26.90	34.0	0.367	20.0	1.70
PE 503-D4336	22.54	478.0	2.51	279.4	1.71
PE 503-D4335	22.22	558.0	2.96	309.4	1.80
PE 503-D4339	21.96	703.7	3.42	399.5	1.76
8356-47-1	25.58	82.9	0.724	47.1	1.76
8356-47-2	24.47	160.7	1.17	91.7	1.75
8356-42	24.36	167.7	1.19	96.4	1.74
8356-48	23.04	356.9	2.10	201.9	<u>1.71</u>
					av. 1.75

Fig. 3. Intrinsic viscosity–molecular weight relationships in THF at 25°C.

TABLE IV

GPC Molecular Weights of Phillips Polybutadiene Samples Using M_{PS}/M_{PBD} Ratio of 1.75

Sample	$M_w \times 10^{-3}$	$M_n \times 10^{-3}$
PE 503-D4338	19.4	18.6
PE 503-D4336	273.2	249.3
PE 503-D4335	318.9	224.1
PE 503-D4339	402.1	358.0

The M_w values agree with the light scattering data in Table II within the experimental limit specified. The GPC M_n values are however higher than the osmometry data, except for sample D4335.

The microstructures of our polybutadiene samples were not determined. They are expected to be similar to those in Table II for Phillips samples.

Styrene–Butadiene Block Copolymer Molecular Weight

The GPC and intrinsic viscosity results of the styrene–butadiene block copolymers prepared by anionic polymerization are shown in Table V. In column 7 of the table are the molecular weights computed by the weighted average method, and in column 8 are the molecular weights computed by the universal calibration method using the intrinsic viscosity data in column 6. The values in column 7 are on the average 5.7% higher than those in column 8. This discrepancy is in agreement with the observation of Ho-Duc and Prud'homme that there are some limited heterocontacts between the unlike segments.

In addition to our own data, the data of Kraus, Naylor, and Rollmann[12] were

TABLE V

Comparison of Styrene–Butadiene Block Copolymer Molecular Weights by the Weighted Average Method and by the Universal Calibration Method

Sample	Type of copolymer[a]	Styrene, wt. %	GPC		$[\eta]$, dl/g	$M_c \times 10^{-3}$ by weighted average	$M \times 10^{-3}$ by universal calibration	% Difference $\dfrac{(M_c - M)}{M} \times 100$
			Peak counts	M_{PS} $\times 10^{-3}$				
8356-16-1	SB pure	47.2	23.85	240	1.226	179	174	2.5
8356-17-1	SB pure	45.4	23.53	290	1.489	214	199	7.4
8356-18	SB tapered	47.5	24.14	201	1.146	150	137	9.1
8356-20	SB tapered	44.4	23.47	303	1.567	222	204	8.9
8356-28	SBS tapered	44.7	23.49	300	1.453	220	216	1.9
8356-29	SBS pure	45.0	23.52	290	1.503	213	198	8.1
8702-17	SBS pure	37.0	24.44	162	0.967	114	112	1.8
C0031-8	SBS pure	63.0	25.73	72.9	0.493	59.3	55.5	6.9
C0031-6	SBS pure	51.4	25.01	114	0.712	86.7	82.9	4.6
								av. 5.7

[a] Pure copolymers were prepared by adding the styrene monomer after butadiene polymerization. Tapered copolymers were prepared by adding both monomers together. Benzene was the solvent and organolithium compounds were the initiators.

TABLE VI
Comparison of Block Copolymer Molecular Weights Based on The Data of Kraus et al.[12]

Type of copolymer	$[\eta]$	$M_w \times 10^{-3}$ by universal calibration	$M_{PS} \times 10^{-3}$	$M_c \times 10^{-3}$ by weighted average	% Difference $\dfrac{M_c - M_w}{M_w} \times 100$
BSB	0.62	51	78	53	3.9
	1.00	97	150	102	5.2
	1.34	154	234	158	2.6
SBS	0.76	54	91	62	14.8
	0.81	82	121	82	0
	1.06	99	157	106	7.1
					av. 5.6

[a] All samples contain 30% styrene by weight.

TABLE VII
GPC and Intrinsic Viscosity Results On Polyisoprene Samples

Sample	GPC		$[\eta]$, dl/g[a]	PIP	M_{PS}/M_{PIP}
	Peak count	$M_{PS} \times 10^{-3}$		$M_w \times 10^{-3}$ by eq. (3)	
8822-39	26.17	59.0	0.427	44.5	1.33
8822-40	23.21	355.5	1.602	262.6	1.35
8822-42	24.71	142.0	0.851	101.5	1.40
8822-44	24.75	139.0	0.835	99.7	1.39
8822-45	24.50	162.5	0.867	124.5	1.30
8822-48	26.10	61.6	0.438	46.6	1.32
					av. 1.35

[a] 25°C in THF.

also examined. The molecular weights derived by Kraus et al. using the universal calibration method are listed in Table VI in the column marked M_w. The polystyrene molecular weights M_{PS} at equal elution volume were calculated from M_w and the corresponding intrinsic viscosities using eq. (3). The Mark–Houwink constants used in this calculation were those reported by Kraus and Stacy[13]: $K = 1.251 \times 10^{-4}$ and $\alpha = 0.717$. From M_{PS}, the corresponding M_{PBD} was obtained by using the 1.75 ratio. In column M_c are the molecular weights calculated from eq. (1), the weighted average method. The difference of the two molecular weights is again about 6% on average.

Styrene–Isoprene Block Copolymer Molecular Weight

The data which led Ho-Duc and Prud'homme to the criticism of the weighted average approximation were on styrene–isoprene block copolymers. In order to compute molecular weights from their data using the weighted average method, polyisoprene calibration is needed. Table VII shows the results on samples of polyisoprene prepared in this laboratory treated in the same manner as the polybutadiene calibration data in Table III.

The data in Table VII were also plotted in Figure 3. The line correlating the intrinsic viscosity and molecular weight is again shown to be parallel to that for polystyrene. The use of a fixed molecular weight ratio for these two polymers

TABLE VIII

Comparison of Styrene–Isoprene Block Copolymer Molecular Weights Based on Data of Ho-Duc and Prud'homme[2]

Type of copolymer	Styrene, wt. %	GPC elution volume, ml	$[\eta]$, dl/g	$M_n \times 10^{-3}$	$M \times 10^{-3}$ by universal calibration	$\dfrac{M - M_n}{M_n} \times 100$	$M_c \times 10^{-3}$ by weighted average	$\dfrac{M_c - M_n}{M_n} \times 100$
SI	48	119.8	0.654	95	122.3	28.7	117.0	23.2
	50	109.1	1.19	221	267.2	20.9	252.0	14.0
	48	92.5	3.60	880	641.7	−27.1	825.0	−6.3
	25	126.3	0.512	58.1	47.9	−17.6	53.8	−7.4
	24	97.5	3.20	530	393.8	−25.7	513.0	−3.2
SIS	65	114.0	0.826	154	222.8	44.7	190.0	23.4
	63	97.9	2.26	510	531.0	4.1	564.0	10.6
	40	111.6	1.23	196	194.3	−0.9	205.0	4.6
						av. 3.4		av. 7.4

in GPC is therefore justified. In THF this ratio is 1.35. Ho-Duc and Pru-d'homme however conducted their experiments in toluene. Their data set contained only three samples of isoprene homopolymer; since toluene is also a good solvent for polystyrene and polyisoprene, we assume that a fixed ratio for the molecular weight of the two polymers is applicable to their data. This ratio, based on their three polyisoprene samples in toluene, was 1.42 and was used in the molecular weight calculation by the weighted average method.

Ho-Duc and Prud'homme presented only the number-average molecular weights of their polymers, presumably by direct measurements, and did not calculate the molecular weights from GPC data. Their data on styrene–isoprene block copolymers are listed in Table VIII together with the molecular weight M by the universal calibration method and the molecular weight M_c by the weighted average method, both derived from their data by us. As shown in the table, the average deviation of M from M_n is +3.4% and M_c from M_n is +7.4%. These numbers are hardly significant enough to conclude whether there were effects of heterocontacts in their GPC data, as the standard deviation of M from M_n is 25.0% and M_c from M_n is 13.8%. The results however do indicate that the weighted average method is more precise.

CONCLUSIONS

The heterocontact effect between unlike segments of block copolymers was detectable in GPC data of styrene–butadiene block copolymers in THF. The GPC data of Ho-Duc and Prud'homme on styrene–isoprene block copolymer in toluene however were not precise enough to show that there was the hetero-contact effect. For their data, the weighted average method, which does not require the determination of intrinsic viscosities, is found to be more precise than the universal calibration method. For broad-distribution block copolymers, the universal calibration method requires on-line viscosity determinations. The precision of on-line viscosity measurement was estimated to be 5% by Grub-isic-Gallot et al.,[5] but the effect of zone spreading on the interpretation of the results was unresolved. Park and Graessley[14] voiced the concern on the lack of precision of viscosity measurements at the high molecular weight tails of the chromatograms and also on the zone spreading effect on the interpretation of the viscosity results. The uncertainty of the universal calibration method for broad-distribution samples is thus likely to be far greater than the 6% error in the weighted average method. In general, for block copolymers in good solvents the weighted average method of determining molecular weights is therefore acceptable; and unless highly precise intrinsic viscosity data are available, it should be preferred over the universal calibration method.

The calibration curves of polystyrene and polybutadiene in THF are found to be parallel as reported earlier. But the ratio of the two molecular weights at equal elution volume was found to be 1.75 instead of the earlier value 2.0. It appears that a fixed molecular weight ratio can also be used for polystyrene and polyisoprene. In THF this ratio is 1.35.

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