Block Copolymer Molecular Weight Determination via Gel Permeation Chromatography: Choosing a Combining Rule

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ABSTRACT: We present a method for accurately determining the true molecular weights of narrow-distribution block copolymers, using only a basic gel permeation chromatograph (GPC) equipped with a refractive index detector and calibrated with polystyrene standards. Our approach is based on the well-known observation that GPC calibration curves for different homopolymers in good solvents are essentially parallel, allowing the curves for different polymers to be described by simple hydrodynamic equivalence ratios r_B versus polystyrene. We present values of r_B, in both toluene and tetrahydrofuran, for various polydiene and hydrogenated polydiene homopolymers commonly incorporated into commercial styrenic block copolymers. These values of r_B must be combined to yield the hydrodynamic equivalence ratio of the block copolymer, from which the block copolymer's true molecular weight can be determined. Three combining rules proposed in the literature are tested against a series of symmetric polystyrene–polybutadiene diblock copolymers of varying molecular weight. A simple linear combining rule accurately represents the results. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 82: 2056–2069, 2001

Key words: gel permeation chromatography; size exclusion chromatography; block copolymer; molecular weight

INTRODUCTION

Gel permeation chromatography (GPC), or size-exclusion chromatography, is the method most widely used today for the characterization of a polymer's molecular weight and molecular weight distribution (MWD). GPC's appeal derives from its speed and simplicity and from the relatively low capital cost of a basic system. The system cost principally depends on the choice of detector(s),

with differential refractive index (RI) detectors being the most inexpensive and robust (and hence widespread). In this article, we describe a method for using a basic GPC system, equipped with only an RI detector, to determine the true molecular weights of narrow-distribution A/B block copolymers.

In the case of block copolymers, GPC analysis is complicated by the fact that elution time or volume depends on both the polymer's molecular weight and the composition.[1–3] It is impractical to obtain and preserve a stock of well-characterized A/B block copolymers which span an adequate range of both molecular weight and composition to directly calibrate a GPC. Rather, one of three options is commonly chosen. The first option is to employ a suitable multidetector system (e.g., refractive index and light scattering) that will pro-

vide the necessary information for an absolute molecular weight determination.[2,4–7] This significantly increases the cost and complexity of the GPC system and is not well-suited to the analysis of polymers of low molecular weights. A second approach is to use the universal calibration curve idea,[8–10] which requires knowledge of the intrinsic viscosity $[\eta]$ of both the polymer to be analyzed and each of the calibration standards. This requires a separate measurement of $[\eta]$ for each analyte polymer; although straightforward, the necessary $[\eta]$ measurement is considerably more time-consuming than the actual GPC analysis, reducing this method's appeal. A third option is to calibrate the GPC with homopolymers of the A and B blocks and then use some sort of combining rule (based on an independent measurement of the block copolymer's composition) to interpolate between the A and B calibration curves. Although this method is the one most commonly chosen, two problems immediately suggest themselves. First, what should the combining rule be? Second, what does one do when only a few standards of one or both of the homopolymers are available, insufficient to construct a complete GPC calibration curve with confidence?

Commercial styrenic block copolymers are typically narrow-distribution diblocks or triblocks of styrene with butadiene or isoprene, synthesized by living anionic polymerization. In some cases, the polydiene block is hydrogenated to improve thermooxidative stability.[11] Although these materials span a rather limited range of chemistries, such polymers constitute 44% of the $2.5 billion U.S. market for thermoplastic elastomers.[12] We present herein a method and the necessary numerical parameters to determine any such block copolymer's true molecular weight, using a GPC running toluene or tetrahydrofuran (THF) as the mobile phase and calibrated with polystyrene standards. In addition, this GPC method is extendable to block copolymers prepared from any two monomers and by any polymerization mechanism which yields a narrow MWD and negligible compositional heterogeneity between chains. Besides anionic polymerization, this could include other living methods such as ring-opening metathesis polymerization,[13] group transfer polymerization,[14] and even controlled free-radical polymerization.[15] In these cases, the minimum set of calibrants required is two: one homopolymer of known molecular weight of each of the blocks, or one homopolymer and one block copolymer of known molecular weight and composition.

EXPERIMENTAL

Materials

Calibration Standards Selection

A series of 20 polystyrene, seven polybutadiene, and six polyisoprene standards from several commercial (American Polymer Standards, Goodyear Chemicals, Polymer Laboratories, National Institute of Standards and Technology, Pressure Chemical Co., and Scientific Polymer Products) and research sources[16] were eventually selected as GPC calibrants. Table I summarizes the characteristics of the various standards.

In the case of polystyrene (PS), the standards were selected from a pool of over 85, which had been collected over the past 30 years. From this pool, we chose standards that were near-monodisperse ($\bar{M}_w/\bar{M}_n < 1.1$) and well-characterized: in most cases, we selected standards that had been characterized by two or more primary methods (e.g., light scattering, membrane osmometry, vapor phase osmometry, sedimentation equilibrium, end group analysis) that produced results which were both self-consistent and in agreement with our own measurements for the breadth of the molecular weight distribution. For example, a standard would be considered well-characterized if the value of $\bar{M}_w$ reported from light scattering and the value of $\bar{M}_n$ reported from membrane osmometry formed a polydispersity index $\bar{M}_w/\bar{M}_n$ which lay within 2% of the value of $\bar{M}_w/\bar{M}_n$ which we obtained by GPC. In a few cases, particularly at lower molecular weights, characterization data from only one absolute method was available. In these cases, we sought consistency between this value and other values reported by the supplier from relative methods (intrinsic viscosity, GPC). In this way, we selected from our large pool of PS standards a smaller set of 30, which was used to construct a calibration curve (fit of log $\bar{M}_w$ versus elution volume for these 30 standards) for the toluene-based GPC system, as described in the following section.

We then checked the PS standards for internal consistency by inspecting the fit residuals, which are the differences between the $\bar{M}_w$ values reported for each calibration standard and the value of $\bar{M}_w$ obtained for that standard from the calibration fit and that standard's measured elution volume. We discarded from the calibrant group any standard whose residual exceeded 5%, provided that this did not create a gap in molecular weight exceeding a factor of 1.5. Finally, we

Table I   Molecular Weight Standards Employed

Polymer Standard	$\bar{M}_w$ (g/mol)	Characterization Methods[a]	Supplier/Polymer ID
		Polystyrenes	
PS 2000	2010	VPO, NMR, LS, IV	Goodyear/CDS-S-9
PS 3000	2840	VPO, IV	Pressure Chemical/12c
PS 4000	3950	VPO, IV, GPC	Pressure Chemical/61110
PS 5500	5520	VPO, LS, IV	Goodyear/CDS-S-10
PS 8000	7820	VPO, LS, IV, GPC	Goodyear/CDS-S-12
PS 10K	10,600	VPO, IV	Pressure Chemical/8b
PS 12K	12,600	LS, MO, IV	Goodyear/CDS-S-3
PS 20K	20,800	LS, MO, SE, IV	Pressure Chemical/2b
PS 30K	30,600	LS, MO, IV, GPC	Polymer Labs/20132-4
PS 50K	48,800	LS, IV, GPC	Polymer Labs/20133-5
PS 80K	79,000	LS, MO, IV	Goodyear/CDS-S-6
PS 95K	93,000	LS, MO	Pressure Chemical/70111
PS 110K	111,000	LS, MO, IV	Pressure Chemical/4b
PS 185K	184,600	LS, MO, SE, IV	NIST/SRM 705
PS 250K	254,000	LS, MO, IV, GPC	Pressure Chemical/50124
PS 400K	405,000	LS, MO, IV, GPC	Pressure Chemical/00507
PS 600K	591,000	LS, MO, IV, GPC	Pressure Chemical/30121
PS 670K	670,000	LS, MO, SE, IV	Pressure Chemical/13a
PS 1.0M	1,100,000	LS, IV, GPC	Polymer Labs/20141-11
PS 1.5M	1,420,000	LS, IV, GPC	Polymer Labs/20142-6
		Polybutadienes	
PB 3000	3010	VPO, NMR, IV	Goodyear/CDS-B-5
PB 8500	8400	GPC	Polymer Labs/21328-3
PB 19K	18,800	GPC	Polymer Labs/21331-2
PB 25K	24,700	LS, MO, IV	Goodyear/CDS-B-4
PB 32K	31,400	GPC	Polymer Labs/21332-3
PB 45K	45,000	LS, MO, IV, GPC	American Polymer Standards/PBU43K
PB 250K	247,100	LS, IV, GPC	American Polymer Standards/PBU240K
		Polyisoprenes	
PI 10K	10,200	VPO, LS, MO, IV, GPC	Goodyear/CDS-1-2
PI 13K	13,200	VPO, LS, IV, GPC	Scientific Polymer Products/582
PI 17K	17,400	LS, MO, IV, GPC	Goodyear/CDS-I-5
PI 85K	85,000	LS	Ref 16/PI 88K
PI 130K	132,000	LS	Ref 16/PI 135K
PI 275K	275,000	LS	Ref 16/PI 283K

[a] VPO = vapor phase osmometry; NMR = nuclear magnetic resonance spectroscopy; LS = light scattering; MO = membrane osmometry; SE = sedimentation equilibrium; IV = intrinsic viscosity; GPC = gel permeation chromatography.

eliminated a few standards simply because they were redundant (very similar molecular weights and elution times) to bring the total number of calibrants down to 20, which provide even and accurate coverage of the elution volume curve. The final calibration curves were generated by using data from only these 20 standards. As shown in Figures 1 and 2, these calibrants cover a range of $\bar{M}_w$ from 2000 to 1.4×10^6 g/mol, with an average molecular weight increment between adjacent calibrants of only a factor of 1.4 in $\bar{M}_w$ (the largest gap in $\bar{M}_w$ is only a factor of 1.6). It is noteworthy that many of the oldest PS standards (Table I), some dating back to the 1960s, won out
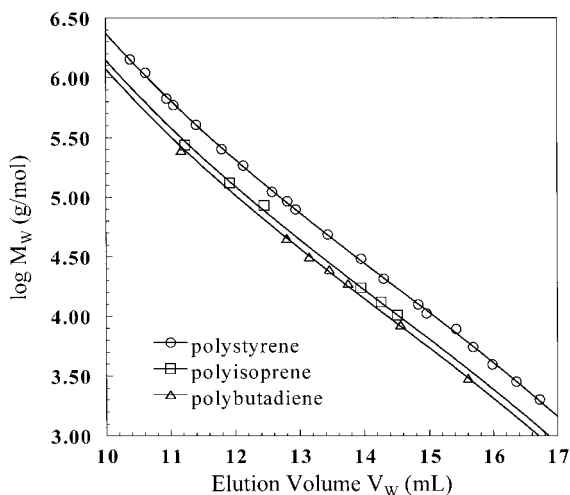
Figure 1 GPC calibration curves, log $\bar{M}_w$, versus elution volume, V_w, for three homopolymers: polystyrene (○), polyisoprene (□), and polybutadiene (△), all measured in toluene at 35°C. Solid curves are cubic fits to the points.

in this selection process over more recently synthesized materials, testifying both to the stable nature of PS and to the enduring value of painstaking molecular weight characterization.

Unfortunately, when selecting standards to generate polybutadiene (PB) and polyisoprene (PI) calibration curves, we could not be so discriminating because of the paucity of commercially available, well-characterized polydiene standards. Besides there being a dearth of suppliers, we encountered two major problems. The most obvious was oxidative degradation; some newly purchased standards were significantly degraded upon arrival, with their GPC traces showing clear evidence of chain branching and scission. The second problem arose from the influence of polydiene microstructure on hydrodynamic volume, and hence, apparent molecular weight. Depending on the polymerization conditions (solvent, temperature, counter ion, added polar modifier), the microstructure of polydienes prepared anionically can vary greatly.[17,18] For example, PI typically has a microstructure comprising 93% 1,4 (mixed cis- and trans-) and 7% 3,4 addition when polymerized via alkyl lithiums in an aliphatic hydrocarbon solvent.[18] Because this is typically how the block copolymers of interest are synthesized, this is the microstructure (high-1,4) desired for the calibrant. However, our analysis by [1]H-nuclear magnetic resonance (^{1}H-NMR) spectroscopy showed that PIs obtained from different suppliers

could have significantly different microstructures. One supplier's PI standards, advertised as being high-1,4, actually contained only 63% 1,4 addition. Standards from this supplier formed a perfectly satisfactory calibration curve by themselves, but differed substantially (factor of 1.2 higher in molecular weight for the same elution volume) from the calibration curve obtained when using truly high 1,4 PIs. All polydiene standards employed in this work had the microstructure anticipated for anionic polymerization in aliphatic hydrocarbons, ca. 93% 1,4 and 7% 3,4 for polyisoprene, and 92% 1,4 and 8% 1,2 for polybutadiene. Overall, the supply of commercially available polydiene standards that met our criteria (undegraded, proper microstructure, internally consistent characterization data) was quite limited, especially for PI. We therefore complemented the three satisfactory PI standards that we obtained from outside with three other polyisoprenes that were synthesized and characterized as part of a previous research project.[16]

Block Copolymer Synthesis

A series of polystyrene–polyisoprene (PS/PI) and polystyrene–polybutadiene (PS/PB) diblock copolymers of varying molecular weights and composition were synthesized by sequential living anionic polymerization under vacuum, styrene block first, with sec-butyl lithium initiator, in cyclohexane at 50–60°C. Solvents and monomers were added to
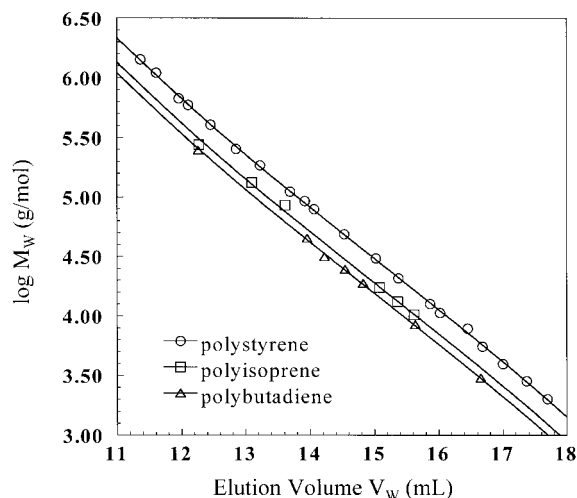

Figure 2 GPC calibration curves, log $\bar{M}_w$ versus elution volume, V_w, for three homopolymers: polystyrene (○), polyisoprene (□), and polybutadiene (△), all measured in THF at room temperature (≈ 23°C). Solid curves are cubic fits to the points.

the reaction vessel by vacuum transfer, after stirring over either diphenyl hexyl lithium (cyclohexane), dibutyl magnesium (styrene), or *n*-butyl lithium (dienes) to remove reactive impurities. After PS block polymerization was complete, a sample was extracted for analysis before the second (diene) monomer was charged to the reactor. The polymerization was terminated with degassed isopropanol. Some of the block copolymers as synthesized contained detectable amounts of terminated first (PS) block. These materials were fractionated with toluene/methanol until homopolymer could no longer be detected in the GPC trace (<0.2 wt %). All block copolymer samples had $\bar{M}_w/\bar{M}_n < 1.05$. ^{1}H-NMR provided the block copolymers' compositions and also indicated that the diene blocks had the expected microstructures (93% 1,4-PI, 92% 1,4-PB).

Gel Permeation Chromatography

Two separate GPC systems were used. The system which employed toluene (Aldrich, HPLC grade) as the mobile phase comprised an isocratic HPLC pump (Waters 515), an RI detector (Waters 410) operated at 35°C, and two 30-cm PLgel 5-μm Mixed-C columns (Polymer Laboratories), which were maintained at 35°C by a column heater (Waters). The system that employed THF (EM Science, spectroscopic grade) as the mobile phase operated at room temperature ($\approx$ 23°C) by using an isocratic HPLC pump (Waters 590), an RI detector (Knauer 198), a multiwavelength ultraviolet (UV) absorbance detector (Waters 490E), and one 60-cm PLgel 5-μm Mixed-C column (Polymer Laboratories). Results reported herein used only the RI detector; however, comparison of the RI and UV traces (at 254 nm) for the block copolymers showed precise superposition, confirming that the chemical composition distribution was negligible. For both systems, the eluent flow rate was maintained at 1.00 mL/min, and injected sample concentrations were 1 mg/mL or lower. The output from each detector was amplified (if necessary), filtered to remove high-frequency noise, converted to a digital signal with a commercial PC-based D/A card, and stored electronically. In-house software was used for data analysis.

A calibration curve was generated by fitting the elution volumes, V_w, of the PS calibrants to a cubic polynomial

$$\log \bar{M}_w = A_0 + A_1 V_w + A_2 V_w^2 + A_3 V_w^3 \qquad (1)$$

where $\bar{M}_w$ is the value assigned to the calibrant based on characterization data provided by the supplier. V_w was determined for each standard by an iterative process: initially, the elution volume, V_p, corresponding to the peak in elution curve for each standard was used in place of V_w in eq. (1) to construct a preliminary calibration curve. To account for the (small) polydispersity present in the standards, each standard was then analyzed with the preliminary calibration curve to determine an apparent $\bar{M}_w$, and the elution volume, V_w, corresponding to this apparent $\bar{M}_w$ determined from the preliminary calibration curve. These values of V_w were then employed in eq. (1) to generate the final calibration curve.

RESULTS AND DISCUSSION

PS calibration standards are available from a wide variety of suppliers, often come thoroughly characterized by absolute methods, span a wide range of molecular weights, are not too expensive, and can be conveniently stored without degradation for many years. However, PS is the only polymer about which all these statements can be made. So before turning to the case of block copolymers, we consider how one might accurately obtain the molecular weights of homopolymers of varying chemistry, when the only extensive set of calibrants available consists of PS.

Hydrodynamic Equivalence Ratios Between Homopolymers

Large Calibration Sets (PB and PI versus PS)

PS, PB, and PI were each used to calibrate both of the GPC systems. The resulting curves are shown in Figures 1 and 2. In both toluene and THF, the calibration curves for the different polymers are essentially parallel, as has been reported previously for both these polymers[19–24] and others.[25] The universal calibration curve idea[8–10] states that polymers of different chemistry eluting at the same time should have identical values of $[\eta]M$; if the Mark–Houwink–Sakurada (MHS) expression is valid, then $[\eta] = KM^a$, and

$$\log M = [\log([\eta]M) - \log K]/(1 + a) \qquad (2)$$

The function $\log([\eta]M)$ versus elution volume is a characteristic only of the GPC system and not dependent on the identity of the polymer. There-

fore, as noted previously,[25] polymers that have the same values of a should have parallel calibration curves, simply shifted from each other by the difference in their values of $\log K/(1 + a)$. For linear polymers in good solvents, the MHS exponent a is generally close to 0.7; reported values in toluene[26] include $a_{PS} = 0.71$ at 35°C, $a_{PB} = 0.71$ at 30°C, and $a_{PI} = 0.74$ at 35°C. Because one would always prefer to use a GPC mobile phase that is a good solvent for the polymer being analyzed, it is reasonable to expect near-parallelism in the calibration curves for any type of polymer successfully analyzed on a particular GPC.[25] We return to this point below, but for now assume strict parallelism of the curves.

If the calibration curves for two homopolymers A and B are strictly parallel in a given solvent, then the two homopolymers are related by a constant hydrodynamic equivalence ratio[21,22] (r_B) such that

$$M_A = r_B M_B \qquad (3)$$

where M_A and M_B are the molecular weights of polymers A and B, which have a common elution volume. The hydrodynamic equivalence ratio r_B can depend on the solvent; if eq. (2) were obeyed with precisely equal MHS exponents for homopolymers A and B, r_B could be calculated from

$$r_B = (K_B/K_A)^{1/(1+a)} \qquad (4)$$

The experimental scatter in reported MHS parameters is rather large,[26] so in practice, measuring the offset between calibration curves (e.g., Figs. 1 and 2) is a much more accurate means of determining r_B.

Because PS is a component of all our block copolymers and is also the choice for calibration standards, we designate PS as polymer A. If an unknown polymer is analyzed by using a calibration curve generated with PS standards, the result obtained is its PS-equivalent molecular weight (M_{PSeqv}), a form in which polymer molecular weights are frequently reported. The ratio of the PS equivalent to true molecular weight is simply r_B, from eq. (3). This ratio holds no matter which moment of the MWD is considered (e.g., $\bar{M}_n$ or $\bar{M}_w$); provided that the calibration curves are parallel, each moment of the PS equivalent and true MWD is related by the same r_B, and the polydispersity index, $\bar{M}_w/\bar{M}_n$, is the same for the PS equivalent and true MWD. However, the PS

Table II Hydrodynamic Equivalence Ratios r_B for Polydienes versus Polystyrene[a]

Polymer	r_B in Toluene (35°C)	r_B in THF ($\approx$ 23°C)
Polybutadiene	1.99	1.96
Polyisoprene	1.68	1.60

[a] Standard deviations in r_B are estimated as ± 0.03 (PB) and ± 0.04 (PI) from the standard error of the fitted A_0 in eq. (1).

equivalent and true values of M can be quite different (r_B greatly different from unity), even for flexible-chain polymers. For example, inspection of Figures 1 and 2 reveals that the PB curve lies approximately 0.3 log units below the PS calibration curve, meaning that $r_B \approx 2$ and PS-equivalent values for PB in toluene or THF exceed the true values by a factor of 2.

Values of r_B were obtained for PB and PI by forcing their calibration curves to adopt the same shape as the curve for PS [same values of A_1, A_2, A_3 in eq. (1)] but allowing for an offset (different value of A_0). These fits are shown as the solid curves in Figures 1 and 2. The value of r_B (Table II) was then simply calculated as the antilog of the difference between A_0 for PB or PI and A_0 for PS. These values can be used directly for the GPC analyses of high 1,4 PI or PB homopolymers in toluene or THF at or near room temperature: after calibrating with PS standards and determining the PS-equivalent MWD (or moments thereof) of the analyte PI or PB, simply divide by the appropriate value of r_B. This eliminates the need to procure and preserve suitable polydiene standards, with all the attendant problems noted in the Experimental section; these values of r_B are valid for the solvents quoted, independent of the choice of columns, detector, pump, flow rate, etc.

Small Calibration Sets (PEP and PEB versus PS) and Error Analysis

As noted above, obtaining a large set of reliable polydiene standards is a challenge. However, the situation for less common polymers is typically even poorer: one may have very few or even just one well-characterized material of a given chemistry. The procedure described above can still be applied: simply obtain the PS-equivalent MWD from GPC and then divide any moment of the PS-equivalent MWD by its true counterpart, known for the polymer of interest, to obtain r_B.

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Table III   Hydrogenated Polydienes: Compositions, Molecular Weights, and Hydrodynamic Equivalence Ratios r_B versus Polystyrene

Polymer Code	Assigned $\bar{M}_w$ (kg/mol)[a]	% 1,2 in Precursor	Toluene (35°C)		THF ($\approx$ 23°C)	
			PS-equivalent $\bar{M}_w$ (kg/mol)	r_B	PS-equivalent $\bar{M}_w$ (kg/mol)	r_B
PEP-L	79.5	—	152.2	1.92	114.0	1.68
PEP-M	139.5	—	286.1	2.05	186.1	1.69
PEP-H	323.4	—	600.6	1.86	424.7	1.61
PEB-38	102.3	38	225.5	2.20	184.3	1.80
PEB-52	84.0	52	161.6	1.92	144.0	1.71
PEB-66	114.0	66	170.3	1.49	154.3	1.35

[a] $\bar{M}_w$ values for the PEPs were determined from GPC on their corresponding PI precursors, and then correcting for the small increase in M after hydrogenation. $\bar{M}_w$ values of the PEBs, given in ref. 27, were determined by light scattering on the PB precursors.

We illustrate this procedure for several saturated polydienes (model polyolefins), which are also components of commercial styrenic block copolymers: poly(ethylene-*alt*-propylene) (PEP), obtained by saturation of high 1,4 PI, and several poly(ethylene-*co*-butenes) (PEBs), obtained by saturation of mixed-microstructure PBs (must be > 35% 1,2 content for the hydrogenated product to be fully soluble at room temperature).

Three PEP specimens of varying molecular weights were obtained[16] by saturation of the three highest M PI standards for which data are shown in Table I. Our best estimates of $\bar{M}_w$ for these materials were obtained from GPC on the PI precursors (using the calibration curve of Fig. 1), and accounting for the modest molecular weight increase on hydrogenation. Three PEB specimens, synthesized and characterized as part of another previous research project,[27] were also examined: one molecular weight of each of three different butene contents (38, 52, 66%; these are the 1,2 contents in the polybutadiene precursor). Each polymer was analyzed on both GPC systems (THF and toluene), its PS-equivalent MWD (and $\bar{M}_w$ value) determined, and r_B calculated from eq. (2); the values are listed in Table III.

For PEP, r_B in THF averages to 1.66, and in toluene to r_B averages to 1.94. The values of r_B measured for the PEBs in both solvents decrease with increasing butene content (as expected, since this decreases the contour length of the polymer backbone). Commercial styrenic block copolymers[11] typically have an E : B ratio of about 60 : 40, meaning that the r_B value for PEB-38 would be appropriate for analysis of such polymers. For both PEP and PEB, r_B in toluene is significantly larger than in THF, indicating that toluene is a better solvent than THF for these polyolefins; for the polydienes, the two solvents yielded rather similar values of r_B (see Table II).

If differences in solvent quality exist between the calibrant (PS) and analyte (PEP or PEB) polymers, this begs the question of whether the underlying assumption of equal MHS exponents is valid. Unfortunately, we could not locate literature values of the MHS exponents for either PEP or PEB (any E : B ratio) in toluene or THF. However, we note that for many other model polyolefins (prepared by hydrogenating polydienes) in THF,[28] values of a range from 0.69 to 0.75 at 30°C. MHS exponents were reported for random EP copolymers (prepared by direct polymerization of ethylene and propylene) in toluene[29] to be 0.79 for temperatures of 20–40°C. It would seem, therefore, that both THF and toluene should be good solvents for PEP and PEB and that their calibration curves should be nearly parallel to that for PS.

However, consider the case where the analyte polymer does indeed have a different MHS exponent a than does PS. In this case, r_B would not be a constant, but would have some dependence on M. Applying again the universal calibration curve idea

$$[\eta]M = K_A M_A^{1+a_A} = K_B M_B^{1+a_B} \tag{5}$$

where K_i and a_i are the MHS coefficients of polymer i. Similarly, at any particular elution time, we may define a corresponding value $r_{B,\text{true}}$

$$r_{B,\text{true}} = \frac{M_A}{M_B} = \left(\frac{K_B}{K_A}\right)^{1/(1+a_A)} M_B^{(a_B-a_A)/(1+a_A)} \quad (6)$$

where M_i is the molecular weight of polymer i corresponding to this elution volume. Note that eq. (6) reduces to eq. (4) when $a_B = a_A$. If only one well-characterized standard of the analyte polymer exists, as with our PEBs, then use of eq. (6) will give a value of r_B which is strictly valid only at the calibration point:

$$r_{B,\text{cal}} = \frac{M_{A,\text{cal}}}{M_{B,\text{cal}}} = \left(\frac{K_B}{K_A}\right)^{1/(1+a_A)} M_{B,\text{cal}}^{(a_B-a_A)/(1+a_A)} \quad (7)$$

We can now consider the magnitude of error that might occur by assuming that $r_{B,\text{true}} = r_{B,\text{cal}}$ across the entire M range. From eqs. (6) and (7), we obtain the following:

$$\frac{r_{B,\text{true}}}{r_{B,\text{cal}}} = \left(\frac{M_B}{M_{B,\text{cal}}}\right)^{(a_B-a_A)/(1+a_A)} \quad (8)$$

Rarely does one expect a GPC system to cover more than about a factor of 1000 in M (e.g., from 1500 to 1,500,000 g/mol). If the polymer B standard lies near the middle of this M range, then the ends of the range lie within a factor of 40 of the calibration point. More commonly, the real range of interest is much narrower; in our experience with styrenic block copolymers, the important molecular weight range spans less than a factor of 25, or a factor of 5 in each direction from the center.

Consider a rather extreme case, where polymer A has $a_A = 0.7$ (as for PS in toluene or THF) and polymer B has $a_B = 0.55$ (recall that θ solvents exhibit $a = 0.5$). If we analyze a B homopolymer having a true molecular weight 40 times larger than $M_{B,\text{cal}}$, eq. (8) yields $r_{B,\text{true}}/r_{B,\text{cal}} = 1.38$, meaning that the true molecular weight of this high-M B homopolymer will be underestimated by 28%. This is a fairly large error, although likely more accurate than defaulting to the PS-equivalent value, $r_B = 1$. However, for the more reasonable case of $M_B/M_{B,\text{cal}} = 5$ and $a_B = 0.6$, $r_{B,\text{true}}/r_{B,\text{cal}} = 1.10$, only a 10% error. This would be quite acceptable for many purposes and is almost certainly more accurate than simply quoting the PS-equivalent M. Of course, for smaller disparities between M_B and $M_{B,\text{cal}}$, the error will be smaller still.

Finally, let us return to this case of PS, PI, and PB discussed in the previous section. Sometimes researchers will obtain (for example) a series of PB and a series of PS standards, construct the two calibration curves, and find that they have slightly different shapes, not simply displaced by a constant factor in log$M$. It is sometimes disputed whether the differences in shape are due to real differences in hydrodynamic volume (MHS exponents) or simply to experimental error in constructing smooth curves from a limited number of somewhat uncertain calibration points (especially for the polydienes). We assert that, at least for PB and PI in toluene and THF, the latter factor is the principal source of the discrepancy and that better results are obtained by force-fitting the polydiene data to the shape of the PS calibration curve (the procedure employed in Figs. 1 and 2), or simply using the r_B values from Table II. Recall that the MHS exponents for PS, PI, and PB are reported to be within 0.03 of each other; although this is comparable to the error in determining such exponents, let us assume here that this difference is real. Applying the method used in Figures 1 and 2 would essentially calibrate the system in the center of the PB or PI molecular weight range, meaning that it is less than a factor of 10 extrapolation to either end of the range of polydiene molecular weights. Equation (8) predicts that for a values differing by 0.03, even a factor of 10 extrapolation produces only a 4% error, within the typical uncertainty in the characterization data for any single molecular weight standard. This suggests that the differences in curve shapes sometimes observed when calibrating a toluene- or THF-based GPC system with PS and PI or PB do not reflect real differences in the calibration curves, but simply the uncertainty in the calibration points. Moreover, forcing the calibration curve for polymer B to follow that for PS (which can be constructed over a much wider range of M, see Figs. 1 and 2) also provides a rational way to extrapolate the calibration curve beyond the range of the polymer B standards.

Block Copolymer Analyses

Combining Rules

Several methods have been proposed for calculating the molecular weight of a block copolymer from information on the properties of its component homopolymers and the block copolymer's composition. When significant composi-

tional heterogeneity exists between chains, the copolymer's chemical composition distribution (CCD)[1–3,6,19,23,30–35] must be considered; but for near-monodisperse block copolymers, the CCD is not broad enough to be significant.[5,36] This simpler case describes typical styrenic block copolymers and is the case that we consider here. Runyon et al.[19,20] first proposed a method for estimating the true M of a block copolymer (M_C) containing A and B blocks, using an empirical logarithmic mixing rule

$$\log M_C = w_A \log M_A + (1 - w_A) \log M_B \quad (9)$$

where w_A is the weight fraction of A in the block copolymer, and M_A and M_B are the M values for homopolymers A and B having the same elution volume as the block copolymer. In other words, M_A and M_B are the molecular weights that would be obtained if the block copolymer's elution time were read using the calibration curves for homopolymer A and homopolymer B, and M_C is simply the weighted average of M_A and M_B, which one would obtain using a lever rule on the usual calibration curve (plot of $\log M$ versus V). If we assume that the A and B calibration curves are parallel, then with the aid of eq. (3), eq. (9) becomes

$$\text{Runyon:} \quad r_C \equiv \frac{M_A}{M_C} = r_B^{(1 - w_A)} \quad (10)$$

where r_C is the hydrodynamic equivalence ratio of the block copolymer. If the A block is PS, then dividing M_{PSeqv} for the block copolymer by r_C yields the desired M_C.

Chang[21,22] instead proposed that a block copolymer with molecular weight $M_C = M_a + M_b$ will have the same elution volume as a homopolymer A with molecular weight $M_A = M_a + r_B M_b$. Here, M_a and M_b are the true molecular weights of the A and B blocks (i.e., $M_a = w_A M_C$) and should not be confused with M_A and M_B. If the calibration curves are parallel (constant r_B), then this reduces to a simple linear mixing rule

$$M_C = w_A M_A + (1 - w_A) M_B \quad (11)$$

from which we obtain

$$\text{Chang:} \quad r_C \equiv \frac{M_A}{M_C} = 1 + (1 - w_A)(r_B - 1) \quad (12)$$

Ho-Duc and Prud'homme[37] started from a more fundamental basis based on an expression for $[\eta]$ of a block copolymer in conjunction with the universal calibration curve idea.[8–10] In a theta solvent for both A and B blocks, $[\eta]_C$ should be given by[38]

$$[\eta]_C^{2/3} = w_A [\eta]_A^{2/3} + (1 - w_A)[\eta]_B^{2/3} \quad (13)$$

where $[\eta]_A$ and $[\eta]_B$ are the intrinsic viscosities of homopolymers A and B having the same M as the block copolymer (i.e., M_A and M_B). Equation (13) was confirmed to be satisfactory for PS/PI diblocks in a range of good and preferential solvents[38,39] as well. Putting this expression into eq. (2) and assuming parallelism of the A and B calibration curves (constant r_B), we obtain

$$\text{Ho-Duc:} \quad r_C \equiv \frac{M_A}{M_C} = \frac{[\eta]_C}{[\eta]_A}$$
$$= [1 + (1 - w_A)(r_B^{2/3} - 1)]^{3/2} \quad (14)$$

Comparing eqs. (12) and (14) shows that they are both special cases of the form

$$r_C = [1 + (1 - w_A)(r_B^d - 1)]^{1/d} \quad (15)$$

where d is the exponent used for the $[\eta]$ combining rule (2/3 for the Ho-Duc method, 1 for the Chang method). Although eq. (15) with $d = 2/3$ was confirmed to be satisfactory for S/I diblocks and S/I/S triblocks in good and preferential solvents,[38,39] the precision in $[\eta]$ measurements does not exclude other values of d, including the value $d = 1$ implied by the Chang method. Indeed, when deviations were observed from eq. (13), they were reported to be in the positive direction,[38] implying $d > 2/3$.

These three combining rules may be evaluated by comparing their predicted values of r_C with those directly measured for suitable block copolymers. The differences between the combining rules are most evident for symmetric block copolymers ($w_A = \frac{1}{2}$) and when the homopolymers constituting the blocks have very disparate hydrodynamic volumes at the same M (large r_B). Therefore, we synthesized a series of symmetric PS/PB diblock copolymers of varying M for this work (Table IV). The true molecular weight, M_C, of each diblock was obtained by taking an aliquot of the PS block prior to addition of the butadiene charge, measuring this block's M by GPC and

Table IV   Diblock Copolymer Compositions, Molecular Weights, and Hydrodynamic Equivalence Ratios r_C versus Polystyrene

Diblock Code	PS Weight Fraction[a]	Results with Toluene as Eluent				Results with THF as Eluent			
		PS Block $\bar{M}_w$ (kg/mol)[b]	Diblock $\bar{M}_w$ (kg/mol)[c]	Diblock PS-equivalent $\bar{M}_w$ (kg/mol)[d]	r_C	PS Block $\bar{M}_w$ (kg/mol)[b]	Diblock $\bar{M}_w$ (kg/mol)[c]	Diblock PS-equivalent $\bar{M}_w$ (kg/mol)[d]	r_C
PS/PB 10/10	0.528	10.6	20.1	31.2	1.55	10.7	20.2	30.6	1.51
PS/PB 20/20	0.494	22.5	45.5	65.7	1.44	22.3	45.1	62.0	1.37
PS/PB 40/40	0.518	39.3	76.0	113	1.50	39.6	76.6	107	1.40
PS/PI 11/10	0.519	11.5	22.2	28.7	1.30	11.4	22.0	28.4	1.29
PS/PI 10/32	0.241	8.6	35.8	52.4	1.46	8.7	36.0	51.3	1.43
PS/PI 3/22	0.128	3.3	25.7	41.6	1.62				
PS/PI 17/9	0.677	17.8	26.3	31.8	1.21				
PS/PI 28/7	0.791	29.7	37.6	41.6	1.11				

[a] Diblock copolymer composition, from ^{1}H-NMR.
[b] $\bar{M}_w$ of the sample of PS first block, from GPC.
[c] Diblock copolymer's true $\bar{M}_w$ = first block $\bar{M}_w/w_A$.
[d] Diblock copolymer's polystyrene-equivalent $\bar{M}_w$.

determining the overall diblock composition by ^{1}H-NMR ($M_C = M_a/W_A$). From the diblock's PS-equivalent molecular weight M_{PSeqv}, we obtain the experimental value of r_C for each diblock as:

$$r_C = \frac{M_{\text{PSeqv}}}{M_C} \qquad (16)$$

These experimental values of r_C are plotted in Figures 3 (toluene) and 4 (THF), superimposed on the values of r_C calculated from eqs. (10), (12), and (14) by using the values of r_B in Table II. Perhaps the first point to note is that the different combining rules do not produce greatly different results for r_C, even for this optimized test case. In particular, the Chang and Ho-Duc combining rules yield very similar values of r_C, meaning that the results are rather insensitive to the choice of d in eq. (15). However, close inspection of Figures 3 and 4 indicates a preference for the Chang and Ho-Duc combining rules over that of Runyon. First, the root-mean-square residual in r_C for the six data points shown in Figures 3 and 4 is 0.073 for both of the Chang and Ho-Duc rules, but 0.100 for the Runyon rule. Second, the data points lie systematically above the line calculated with the Runyon rule (5 of 6). Finally, all the data points lie within 2.5σ of the Chang and Ho-Duc curves, but lie as much as 3.5σ away from the Runyon curve, where σ is our estimate of the standard deviation in the experimentally measured r_C. For

comparison, Figure 5 shows the measured and calculated r_C in toluene for PS/PI diblocks of varying composition. Because r_B for PI is smaller than for PB, the deviations between the combining rules are smaller, and each of the data points lies within a little over 1σ from all three of the calculated curves.

The results presented here do not permit a clear discrimination between the Chang and Ho-Duc rules; indeed, eq. (15) with any value of d lying between $0.6 < d < 1.1$ gives a root-mean-square deviation in r_C of less than 0.075 with experiment, although the deviation grows rapidly for values of d outside this range. Trying to determine the best value of d in eq. (15) does not seem a particularly worthwhile endeavor for two reasons. First, the effect of this parameter is small; even for the case of $r_B = 2$ and $w_A = \frac{1}{2}$, the predictions for r_C with $d = 0.6$ and $d = 1.1$ agree to within 3%. Second, even for theta solvents, eq. (13) hinges on the assumption that A-B contacts are neutral (that is, energetically equivalent to A–A and B–B contacts) so that ideal chain statistics are obtained. Deviations from this assumption will most likely occur to different extents depending on the chemistry of the system (e.g., the identity of A and B), and hence the best value of d to use may vary slightly from system to system, with those having more unfavorable A–B contacts requiring slightly larger values of d. Because any value of d from 0.6 to 1.1 appears to
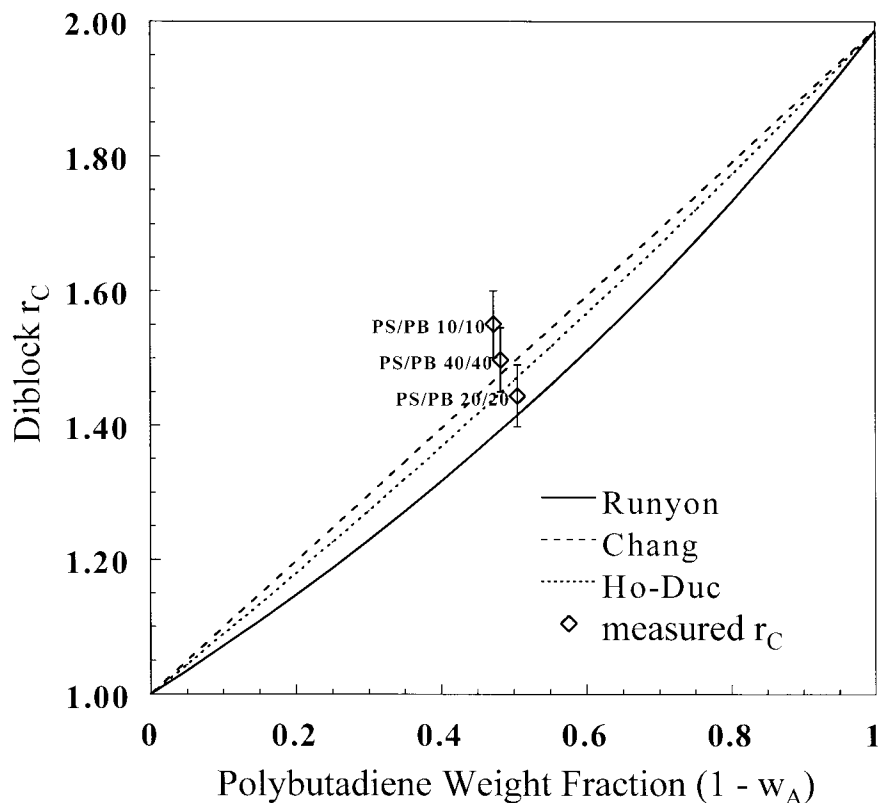
Figure 3 Hydrodynamic equivalence ratio r_C for PS/PB diblocks versus weight fraction PB ($= 1 - w_A$) in toluene at 35°C. The curves are calculated from the combining rules of Runyon et al.[19,20] (—), Chang[21,22] (– – –), and Ho-Duc and Prud'homme[37] (- - - -) by using $r_B = 1.99$. The data points ($\diamond$) represent the measured values of r_C for each diblock. Error bars are $\pm 1\sigma$ based on diblock composition error (± 0.5 wt %) and uncertainty in determining the diblock's PS-equivalent M ($\pm 2\%$).

work equally well, at least for the styrene–diene diblocks studied here, we have chosen to adopt the Chang rule [eq. (12)] in our own work because of its simplicity.

Generalization to Nonstyrenic Block Copolymers and to Multiblock Architectures

In the above equations, we designated polystyrene as polymer *A* (or the *A* block), both because it is the polymer of choice for calibration and because it is a component of all the block copolymers described herein. However, these equations are readily extended to nonstyrenic block copolymers, even when the GPC is still calibrated with PS standards. All that is needed is the hydrodynamic equivalence ratios r_B versus PS for both blocks (e.g., PB–PI diblocks could be analyzed with the r_B values in Table II, or PEP–PEB diblocks with the values in Table III). The general form of eq. (12) for an arbitrary *A/B* diblock is

$$r_C \equiv \frac{M_{\text{PSeqv}}}{M_c} = r_A + (1 - w_A)(r_B - r_A) \quad (17)$$

where r_C is still the hydrodynamic ratio for the diblock versus PS and r_A is the hydrodynamic equivalence ratio for the homopolymer of block *A* versus PS (i.e., it is the value of r_B which corresponds to the block denoted *A*).

We also note that all three combining rules evaluated above make no explicit assumption about how the *A* and *B* sequences are arranged, save that the block copolymer is linear; linear *A/B* diblocks, *A/B/A* triblocks, and *A/B/A/B/A* pentablocks would all have the same calculated values of r_C. This is equivalent to assuming that $[\eta]$ for a block copolymer is insensitive to how the block sequences are distributed along the chain, which was verified to within experimental error for PS/PI diblocks and PS/PI/PS triblocks.[39] This approximation appears reasonable provided each of
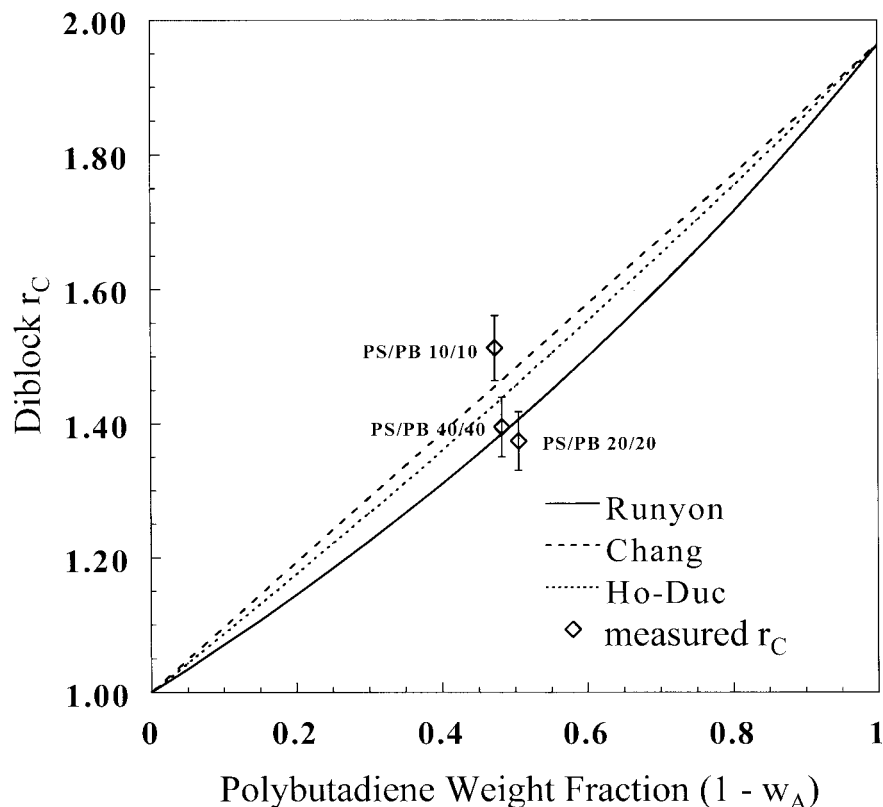
Figure 4 Hydrodynamic equivalence ratio r_C for PS/PB diblocks versus weight fraction PB ($= 1 - w_A$) in THF at room temperature ($\approx 23°C$). The curves are calculated from the combining rules of Runyon et al.[19,20] (—), Chang[21,22] (– – –), and Ho-Duc and Prud'homme[37] (- - - -) by using $r_B = 1.96$. The data points ($\diamond$) represent the measured values of r_C for each diblock, with $\pm 1\sigma$ error bars.

the blocks is sufficiently long to exhibit random-walk chain statistics; indeed, this is an assumption underlying eq. (13).

Determination of r_B from Block Copolymerization

Finally, we note that r_B can be determined for an unknown homopolymer if an A/B diblock can be synthesized with another monomer whose r_B value versus PS is known (designated as block A below, so r_A is known and r_B is sought). Precision on r_B is best when the block copolymer is rich in B (i.e., $w_A < ½$). The diblock's composition must be determined (e.g., by ^{1}H-NMR), and the PS-equivalent M both of the diblock (M_{PSeqv}) and of a first block sample [either $M_{a,\mathrm{PSeqv}}$ or $M_{b,\mathrm{PSeqv}}$, depending on whether the known (A) or unknown (B) block is polymerized first] must be obtained from GPC. If the A block is the first block, then working from eq. (17), the expressions for r_B and the true molecular weight of the diblock M_C are

$$M_C = \frac{M_{a,\mathrm{PSeqv}}}{r_A w_A} \qquad (18)$$

$$r_B = r_A + \frac{(M_{\mathrm{PSeqv}}/M_C) - r_A}{1 - w_A} \qquad (19)$$

However, in some cases the chemistry is such that the unknown (B) block must be polymerized first. In this case, starting again with eq. (17), the expressions are

$$r_B = r_A\left(\frac{w_A}{1 - w_A}\right) \frac{M_{b,\mathrm{PSeqv}}}{M_{\mathrm{pSeqv}} - M_{b,\mathrm{PSeqv}}} \qquad (20)$$

$$M_C = \frac{M_{b,\mathrm{PSeqv}}}{(1 - w_A)r_B} \qquad (21)$$

This approach allows an estimate of r_B to be obtained without even a single well-characterized
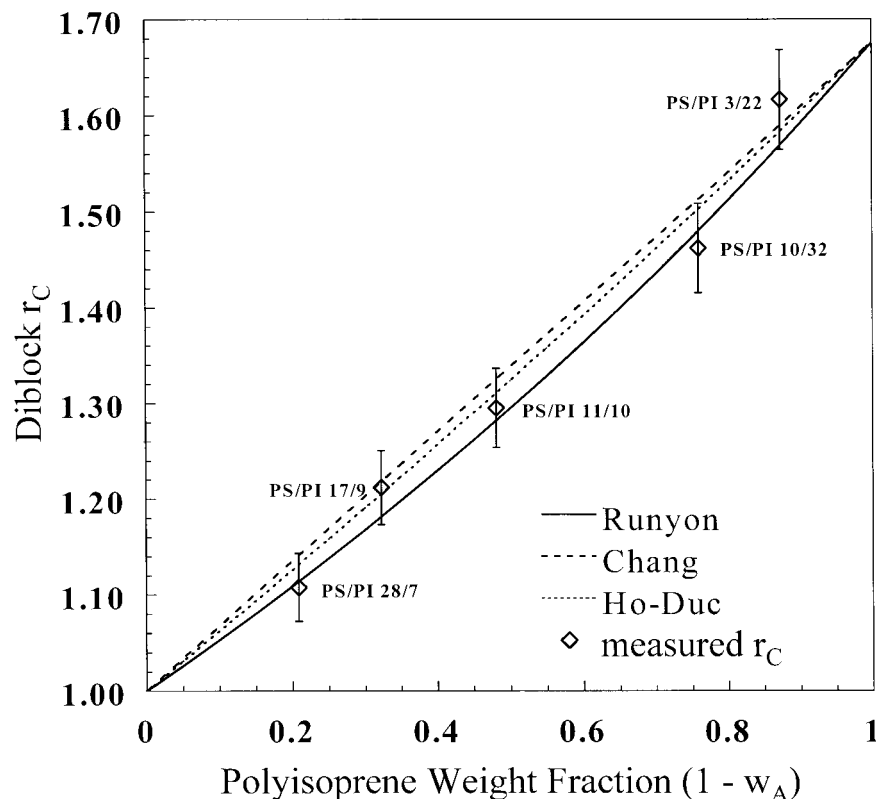
Figure 5   Hydrodynamic equivalence ratio r_C for PS/PI diblocks versus weight fraction PI ($= 1 - w_A$) in toluene at 35°C. The lines are the curves calculated from the combining rules of Runyon et al.[19,20] (—), Chang[21,22] (– – –), and Ho-Duc and Prud'homme[37] (- - - -) by using $r_B = 1.68$. The data points ($\diamond$) represent the measured values of r_C for each diblock, with $\pm 1\sigma$ error bars.

standard of polymer B, although it can be used in only a limited number of cases, those where the A and B polymerization chemistries are compatible and yield narrow-distribution block copolymers. We have determined r_B in this fashion for poly-(ethylidene norbornene), which can be polymerized by ring-opening metathesis polymerization and can constitute the first block of a diblock with polycyclopentene.[40] Polycyclopentene accurately follows the PB calibration curve because of its close structural similarity.

CONCLUSION

We have shown that accurate measurements of the true molecular weights of linear block copolymers can be obtained by using only a basic GPC system, having an RI detector and calibrated with PS standards. Our approach requires that the hydrodynamic equivalence ratio r_B between the two blocks and PS be known in the solvent used

as the GPC mobile phase. We measured r_B in toluene and THF for the most common constituents of styrenic block copolymers: PI, PB, PEP, and PEB. We expressed the previously published combining rules of Runyon, Chang, and Ho-Duc in terms of r_B and tested these rules against a series of symmetric PS/PB diblocks. The Chang and Ho-Duc rules, which reduce to mathematically similar forms, could not be discriminated between; however, both were shown to yield more accurate results than the widely used method of Runyon. Finally, we discuss how this method can be used to determine r_B for an analyte polymer B when no homopolymer molecular weight standards of B are available but when an A/B diblock can be synthesized.

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