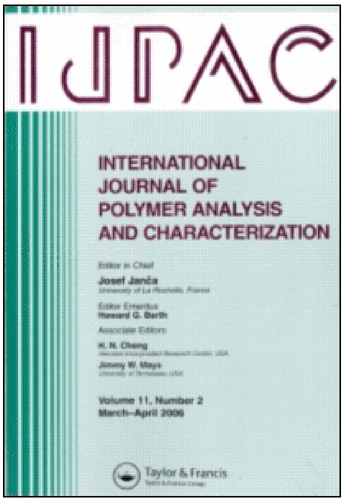

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Characterization of Low-Molecular-Weight Polymers: Failure of Universal Calibration in Size Exclusion Chromatography

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Characterization of Low-Molecular-Weight Polymers: Failure of Universal Calibration in Size Exclusion Chromatography

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Accurate measurement of molecular weights for polymers in the 500–5000 molecular weight range requires considerable care. Absolute methods such as membrane osmometry or light scattering are generally imprecise because of membrane permeation or low scattering intensity. Many polymers are too fragile to be studied by mass spectrometry. Other techniques, such as vapor phase osmometry, cryoscopy, and ebulliometry require calibration and data replication if accurate molecular weights are to be obtained. Size exclusion chromatography (SEC) also requires calibration but can be a very rapid and accurate method if proper calibration can be achieved. SEC calibration is now often achieved via "universal calibration" (UC), which is based on the premise that polymers with the same hydrodynamic volume will have the same SEC retention time. At very low molecular weights, the UC approach is clearly invalid since intrinsic viscosities can become negative for certain polymers. We demonstrate here that the invalidity of the UC concept extends well outside this molecular weight region, up to at least 1000 molecular weight for the polystyrene (PS)/polyisobutene (PIB) case. We have also tested whether PS, PIB, and *n*-alkanes elute at equivalent radii of gyration, R_g. This approach leads to somewhat smaller errors than UC, but also is not adequate for accurate work. Another SEC issue in this molecular weight range, with the commonly used differential refractive index (DRI) detector, is the variation of the detector response with molecular weight. This variation is proportional to $1/M_n$ and, if neglected, can cause substantial overestimations of M_n (e.g., 10–25%) in the SEC analysis of polydisperse samples in THF solvent. Theoretical and experimental data are presented for PS, PIB, and polymethylmethacrylate, quantifying the error. Errors in light scattering weight-average molecular weights caused by the RI variation can also be significant and depend on the molecular weight distribution; accurate results can be obtained, but only if M_n is accurately known, even if dn/dc is measured on the sample under study.

KEY WORDS Universal calibration, size exclusion chromatography (SEC), polystyrene, polyisobutene, n-alkanes, molecular weight, refractive index, vapor phase osmometry (VPO).

INTRODUCTION

Characterization of low-molecular-weight polymers is a problem of both fundamental and practical interest. Low-molecular-weight polymers (molecular weights in the few hundred to few thousand range) represent a significant portion of the total commercial polymer market, with applications such as plasticizers, detergents, food additives, and lubricant additives. Most of these polymers have large polydispersities; control of both the number-average molecular weight and the polydispersity is often key to achieving optimum performance. Although there is a fairly large body of literature on low-molecular-weight polymers, systematic studies covering the range from oligomers to high-molecular-weight polymers are less common. Because of the polydisperse nature of most low-molecular-weight commercial polymers, a general understanding of structure–property relationships over a broad molecular weight range is required for accurate characterization and ultimate property optimization.

Number-average molecular weights (M_n) of low-molecular-weight polymers are often determined from colligative property measurements [1–3]. The most commonly practiced method is vapor phase osmometry (VPO), which is based on the lowering of solvent vapor pressure by a solute. Although VPO can provide quite accurate M_n values, speed and precision are often issues in routine application in a commercial setting. In any case, VPO does not provide any information on the weight-average molecular weight (M_w). Size exclusion chromatography (SEC) has become the preferred characterization method because it is fast and precise and because it can provide M_n, M_w, and other characteristics of the molecular weight distribution [1–3]. Nevertheless, SEC must be calibrated and inevitably relies on one or more primary methods of molecular weight determination.

A key complication in the characterization of low-molecular-weight polymers is that many properties that may be assumed constant in the analysis of high-molecular-weight polymers are not constant in the low-molecular-weight regime. For example, refractive index and density both show significant variation with M_n (generally linear in $1/M_n$) [4–6]. The variation of refractive index with molecular weight is of particular importance, since it impacts the accuracy of molecular weight averages obtained from both SEC (with a differential refractive index, DRI, detector) and light scattering [1, 7]. The intrinsic viscosity dependence on molecular weight also becomes quite complicated at low molecular weights. In fact, polystyrene exhibits among the most complicated behaviors observed for nonpolar polymers [8–10]. Empirical viscosity molecular weight relationships (e.g., the Mark-Houwink equation) cannot be extended into the low-molecular-weight range (below about 1000) where, in extreme cases, intrinsic viscosities can become negative [11]. As a result, "universal" SEC calibration procedures based on such relationships [12] are suspect when applied to low-molecular-weight polymers.

In this paper, we discuss a range of issues associated with accurate molecular weight measurements in the low-molecular-weight region. The variation of refractive index with molecular weight is discussed for polystyrene (PS), polyisobutene (PIB), and polymethylmethacrylate (PMMA), with examples given for the effect on SEC and light-scattering measurements. An accurate, intrinsic viscosity-molecular weight database is given for PIB, as well as its relationship to n-alkanes and PS, from the PIB dimer up to molecular weights of 10^5. These results, combined with extensively cross-checked molecular weight measurements, lead to a demonstration of the failure of SEC universal calibration at low molecular weights for these systems. The radius of gyration, determined from experiment and theory, is also examined as an SEC separation parameter.

EXPERIMENTAL

Solvents:

For suspended-level viscometry, tetrahydrofuran (THF, Baker Analyzed R), was dried over CaH_2, then distilled after refluxing over metallic sodium for at least 48 h. The first 150–200 mL of the distillate, representing about $\frac{1}{4}$ of the total volume, were discarded. The remainder was stored over sodium and distilled just prior to use. For SEC, THF (Burdick and Jackson, high-purity solvent) was for chromatography and online viscosity measurements without further treatment. The H_2O specification for the THF was less than 0.05 wt %. Some suspended-level viscometry experiments were conducted with THF without further treatment; the results were identical to those obtained with carefully dried THF. Thus we had no indication that H_2O absorption in THF influenced viscosity measurements. The literature suggests that at least several tenths of a percent H_2O would need to be present to cause a significant change in intrinsic viscosity, especially at low molecular weight [13]. Nevertheless, care was taken in all chromatographic and viscometric procedures to minimize exposure to the atmosphere.

For viscometry and light scattering (LS), heptane (Burdick and Jackson, high-purity solvent) was purified with the same distillation procedure, as was the benzene (Baker, reagent grade) used in a limited number of viscosity measurements for M_w cross-checks.

For VPO, toluene was used in the cited commercial laboratories following their own protocol. For our own work, we employed reagent grade toluene from Burdick and Jackson without further treatment.

Materials:

Polystyrene standards were purchased from Polymer Laboratories (PL) covering the molecular weight range 162–100,000 and containing an *n*-butyl end group from the anionic initiator. They are designated PLX, where X is the peak molecular weight assigned by PL, for example, PL580. PS dimer (degree of polymerization, DP = 2) and PS trimer (DP = 3), each with a *n*-butyl end group, were obtained from Polymer Standards Service (PSS, Mainz). PS dimer, trimer, and tetramer were also obtained in small quantities by fractionating (preparative SEC) a low-molecular-weight PL standard (PL580); the dimer and trimer were identical to those supplied by PSS (with respect to intrinsic viscosity and SEC retention time). These samples are designated PSX, where X is 266, 370, and 474. Other polystyrene standards from various sources (including NBS706) were used for comparative purposes. PMMA standards were obtained from PL.

PIB samples came from a variety of sources. With the exception of purchased oligomers, all had their origins in Lewis-acid catalyzed, cationic polymerizations. Narrow standards were obtained from PSS (600–100,000) designated PSSX. Broad and narrow standards (300–250,000) were obtained from American Polymer Standards (APS, Mentor, Ohio), designated APSX. Several of the identical narrow PIB standards available from PSS are also available from APS. Polydisperse isobutene homopolymers were synthesized in our laboratories and fractionated by preparative SEC (hexane solvent) into fractions, most having $M_w/M_n < 1.2$; these fractions covered the M range 400–40,000 (designated PIBn, with $n = 1$ to 15). The parent polydisperse PIB ($M_n = 1750$, $M_w/M_n = 2.5$; see below) for the lower portion of this molecular weight range is designated PPIB1. One other polydisperse sample (PPIB2) of commercial origin ($M_n = 1260$, $M_w/M_n = 2.0$; see below) was also used. Two narrow distribution samples of PIB were prepared by "living" cationic polymerization (Professor R. Faust, University of Lowell); quoted M_n values from Professor Faust for these samples (VPO) were 2300 and 2500. These samples are designated PIBF1 and PIBF2, respectively. The dimer, trimer, and tetramer of isobutene (DP = 2, 3, 4) are available from Aldrich, TCI America, and Wiley, respectively. Infrared, NMR, and GC mass spectrometry were performed on several of the PIB samples to confirm their homopolymer structure and chemical purity. Commercial PIB ("polybutene") contains varying amounts (typically < 5%) of copolymerized 1-butene. For example, infrared spectroscopic analysis of PPIB2, based on calibration with PPIB1 and poly(1-butene) mixtures, yields a butene content of about 4%; APS6K, also of commercial origin, is 3% butene by the same analysis. Low DP standards derived from commercial material are available from PSS but were not used because of the presence of significant amounts of oxygenated polybutene, which affected viscosity and refractive index measurements. These standards are suitable for SEC calibration, since their peak retention times are assignable to the non-oxidized portion of these samples, and are in good agreement with our peak retention time data for PIB materials described above. Based on our work, the physical properties of these polybutene copolymers (including SEC peak retention times) are essentially indistinguishable from those of the PIB homopolymers employed in the majority of this work (see also reference 14). Further discussion of this point is included in the section dealing with refractive indices.

Instrumentation and Experimental Protocol

Intrinsic viscosities $[\eta]$ were measured in a suspended-level viscometer and online with the SEC instrument. For the suspended-level measurements relative viscosities η/η_s were determined at 25°C and 30°C in THF by using a Schott-Geratte automatic viscometer. The solvent flow time is ~ 110 s for the majority of the measurements reported here and ~ 180 s for the remainder. The flow time was measured with precision of 0.01 s. Relative viscosities were typically in the range 1.1 to 1.5; for low DP polymers, values as low as 1.03 were included in the analysis. For both PS and PIB, $[\eta]$ results at 25°C could not be distinguished from those at 30°C, and are all labeled 30°C for simplicity. For selected samples, intrinsic viscosities were determined in heptane (30°C) and benzene (25°C) solely for the purpose of crosschecking M_w assignments with other workers.

Intrinsic viscosities were obtained by extrapolation of $(\eta - \eta_s)/\eta_s c$ to zero concentration, via the Huggins relation:

$$(\eta - \eta_s)/\eta_s c = [\eta] + K_h[\eta]^2 c$$

The $[\eta]$ values obtained on three samples (PL2450, PL10K, and NBS706) were used to calibrate the Viscotek Differential Viscometer Model 110 (though cross-checks were also made on several PIB samples). The Viscotek operated at 30°C with a flow rate of 0.55 mL/min. A differential pressure transducer (DPT) setting of 0.243 in the Viscotek software matched the Viscotek and suspended-level viscometers. The flow rate provided by the chromatograph pump, the split of the solvent stream to the bridged viscometer (almost exactly 50% to each), and the reproducibility of the injection volume were good enough to provide data accurately to about 1–2% relative standard deviation. All data were obtained at least in duplicate. The data were analyzed with the Viscotek software package TriSEC–GPC 2.00, "Windows" version. The injected solution concentration was varied to produce a ΔP of about 15–50 Pa. The product of injected concentration and intrinsic viscosity was maintained at about 0.1. The concentration in the eluant, reduced by SEC fractionation, was about a factor of 20 lower at the concentration maximum in the chromatogram. The online viscometer software combines the Huggins and Kramer's definitions so that an intrinsic viscosity was calculated from a single concentration at this low concentration [1]. In the data reported here the online viscometer was used only to measure $[\eta]$ for the whole polymer, so that interdetector and SEC band-spreading corrections are irrelevant.

The chromatography was performed with a Waters 710B and 712B autosampler–injector and model 410 differential refractometer with THF as solvent at 32°C. Sulfur was employed as an internal standard to correct for small variations in flow rate. Data were analyzed with CALS software from Beckmann instruments; Viscotek software gave equivalent results. Polymer solutions were made by weight with conversion to units of weight/volume via 0.886 g/mL as the density for THF, and PIB and PS densities from formulas given in the following section. The solutions were prepared open to the laboratory atmosphere with about a 30 s exposure of the THF to moisture. We elected to use THF without antioxidant, since the commonly employed BHT antioxidant elutes close to the PIB tetramer and PS trimer and can interfere with the analysis of polydisperse samples if solution and solvent are not well matched in their BHT concentrations. No changes in results were observed for solutions stored at 20°C for periods of several days. The solutions were exposed to fluorescent light in benchtop storage and were sometimes stored for longer periods, refrigerated at 5°C in the dark.

Two column sets were employed for the bulk of this work. One consisted of three PL "linear" columns with a PS exclusion limit of 400,000 (designated Linear columns), and the other, also from PL, employed 2 × 50Å, 2 × 100Å, and 1 × 1000Å columns with a PS exclusion limit of 30,000 (designated High Resolution columns). All columns are 7.5 × 300 mm. Calibration was performed employing a subset of the narrow standards described above. For selected samples, molecular weights assigned by the suppliers were checked by VPO, light scattering, refractometry and viscometry (heptane, benzene, and THF) for consistency with our data and literature data. The High Resolution column set was employed in order to resolve the oligomers of PS and PIB up to DP = 9 for PS and DP = 14 for PIB. With the individual peaks for authentic oligomers as benchmarks, it is easy to construct a calibration up to about $M = 800$ even if the molecular weight of the total sample is not known and even if the "standard" is not of narrow molecular weight distribution. Because of the low exclusion limit and the more complicated shape of the calibration curve for the High Resolution column set, this set had limited utility in analyses of polydisperse samples. The Linear column set was employed for those analyses. Since both column sets yielded apparent polydispersities of less than 1.01 for PS and PIB oligomers, no corrections for SEC band spreading were deemed necessary. For molecular weights below 1000, even for narrow standards, the injected amount of polymer could be varied from 0.5 to 3 mg (100 μl of 0.5 to 3% solutions) with no measurable effect on elution time. We regard these results to be concentration independent. For molecular weight above 10^4, a small concentration dependence was observed. For example, at 20,000 g/mol on the Linear Column set, PIB and PS both displayed a concentration dependence of about 0.01 min-mL/mg, which would correspond to a variation of 2–3% in peak molecular weight in both cases. However, because calibrants and unknowns were run at similar concentrations, the error is essentially zero. Since our interests are primarily in the low-molecular-weight region and, for the study of universal calibration, comparative in any case, corrections for this concentration dependence were not made.

Once calibrations were constructed, internal consistency was attained by having the peak molecular weight (M_p) values determined from SEC analysis of the standards be within 2% of the value originally assigned in constructing the calibration (throughout the M range for the Linear columns; up to 5,000 g/mol for the High Resolution columns). There is considerable discussion in the literature as to what molecular weight average corresponds to M_p [1, 15–16]. In the absence of instrumental band spreading, for a mix of linear and branched or copolymer species of identical hydrodynamic volume, it has been shown [16] that if $[\eta]$ is measured on line, the appropriate M in UC is M_n. This is not the case for conventional calibration with narrow distribution linear samples; M_p can vary from less than M_n to greater than M_w, dependent on the distribution shape. For our data, M_p falls most often at about 0.9 M_w, in the vicinity of M_v. That is the internally consistent experimental result, that is, it is what an analysis of a narrow standard produces when it is analyzed on the calibration curve of which it is a part. Also if the axes are transformed so that the chromatogram is presented on a linear M axis, with the appropriate Jacobian of the transformation made, the peak can also shift. Our M_p values are defined in terms of the observed peak retention times for the polymer in THF on a column set that has a log M_p relationship essentially linear in retention time. It should be noted that M_p will shift slightly depending on whether or not corrections are made for the variation of refractive index with molecular weight (see following section). There are only a few samples at low molecular weight where this correction is of any consequence for M_p assignment. If a sample has multiple peaks of similar size, the correction can make the choice jump from one oligomer peak to another. All our M_p values are corrected for the refractive index variation, as are our SEC-derived M_n and M_w values.

Low angle laser light scattering (LALLS) intensities were measured with a Chromatix KMX-6 photometer (633 nm) at 27 ± 0.5°C in heptane. The nominal angle of scattering was 6–7°. The actual value calculated, from the refractive index of heptane (1.3803 at 633 nm and 27°C), was 4.705°. A 0.2-mm aperture was used. The output signal from the photomultiplier was recorded on a strip chart, and the scattering intensity was taken at the baseline (lowest scattering) of the fluctuating

(~ 0.5%) signal. Measurements were usually performed on a series of 4–8 different concentrations, chosen to be lower than c^* (i.e., $[\eta]c < 1$) and to have the total scattering R' at 2–6 times the Rayleigh ratio of heptane, $R = 5.64 \cdot 10^{-6}$ cm^{-1}.

The scattering intensities for the solutions were converted to Rayleigh ratios, and the polymer contribution, $\Delta R = R' - R$, was plotted as $(Kc/\Delta R)^{1/2}$ vs. c to minimize the effects of curvature caused by the third virial coefficient:

$$(Kc/\Delta R)^{1/2} = M_w^{-1/2}(1 + A_2 c M_w)$$

where K is a known function of n, wavelength, and dn/dc. M_w was calculated from the intercept of $(Kc/\Delta R)^{1/2}$ vs. c. For polydisperse samples where dn/dc is a function of M_n, this M_w value must be corrected to obtain a true result [17]. All solutions were filtered through a 0.22-μm nylon filter (Fisher Scientific Co.). For a few samples, M_w was measured via multi-angle LS and Zimm analysis. The specific refractive index increment was measured with a KMX-16 differential refractometer at 27°C and 633 nm. Calibration and operation followed the manufacturers instructions.

Three PIB samples were analyzed by small angle neutron scattering (SANS) for determination of the root-mean-square radius of gyration (R_g), which will be a z-average in this scattering experiment (R_{gz}). The measurements were carried out on the 8-m instrument at the National Institute of Standards and Technology (NIST). The neutron wavelength was 10.5Å, and the sample to detector distance was 3.6 meters. The q range was 0.01 to 0.1 Å^{-1}. A secondary NIST silica standard was used for absolute intensity calibration. The solvent was deuterated decane. Small adjustments (5–10%) were made to obtain the desired average, R_{gw}, from the measured R_{gz} (based on SEC data for these same samples). Rough estimates of M_w from SANS were in reasonable agreement with LS (±15%).

For refractive index measurements on the neat polymers, an Abbe 3L refractometer was employed at 25.0°C and 589 nm (sodium D line). The instrument was factory calibrated. Heptane (Burdick and Jackson, high-purity grade) was used as a control and consistently gave 1.3853 ± .0001 as a reference value for the instrument during all of the polymer measurements. That heptane value is consistent with the literature [18]. Although measurements were made over the temperature range 15–60°C, most reported results are for 25°C.

Polymer refractive index (n_p) is easily perturbed by residual solvent, degradation and oxidation products. After considerable study, we determined that our narrow distribution PIB samples with M_n below about 5000 had to be "dried" under vacuum for 24 hours (~ 1 mm Hg) as a thin, < 0.05-cm film, at 60–80°C to remove residual solvent (hexane from the fractionation process) and to obtain constant n_p values. Typically n_p increased by 0.0005 to 0.0010 during this period. For the higher M_n samples, drying at 80°C for 10 or more days was required to achieve near constant n_p values. For example, PIB15 ($M_n \sim 35{,}000$) increased with an approximate $1/\sqrt{t}$ dependence from 1.5074 to 1.5087 after 12 days. "Drying" at 100°C or above for extended periods of time (e.g., 24 hours) lead to erratic results (increasing then decreasing n_p) which we confirmed by SEC to be due to either thermal or oxidative degradation. For some critical samples (such as PIB15), the drying process was carefully monitored by SEC to ensure no degradation was taking place. Polydisperse samples which had not been exposed to solvent, underwent no change in refractive index with the 60°C treatment and apparently have been appropriately dried in their manufacture. Thus refractive index is an easy way to get a quick estimate of M_n in the low-molecular-weight regime, but only if the samples are appropriately prepared prior to measurement. The preparation is more stringent than is necessary for SEC or VPO, since very small and volatile molecules are not detected by those techniques. Obtaining good optical contact with the refractometer prism for the higher-molecular-weight PIB samples ($M_n >$ 50,000) also posed some problems. Firm manual pressure exerted by hand on the upper prism was needed to obtain a good "line." A polarizer can be employed to check for orientation, which must be avoided.

Vapor phase osmometry (VPO) was performed on a Wescan instrument model 233, employing toluene as solvent at 50°C. The instrument was operated according to the manufacturers instructions and in accordance with ASTM D3592. Calibration was performed with tetracosane ($M = 338$, $K = 2150 \pm 40$) and sucrose octaacetate ($M = 678$, $K = 2155 \pm 40$). As indicated, the two calibrants yielded the same calibration constant within $< 1\%$ with an overall uncertainty of about 2%. Based on an intercomparison of these standards and the results by Burge [19] at high molecular weight, VPO can give accurate results with no bias versus true molecular weights. For the sample measurements described herein, three or four concentrations were employed over the range 5–30 g/kg solution. Precision for the sample determinations was about $\pm 5\%$, compared to $\pm 2\%$ for the calibrants, due to the limited quantity of samples available for these measurements. VPO measurements were also performed by two commercial laboratories (Huffman and ARRO) using their own procedures.

In general, colligative property measurements need to be extrapolated to zero concentration to eliminate non-ideal effects [1–3]. For VPO the operating relationship is

$$\Delta R/c = K\left(1/M_n + A_2 c + A_3 c^2 \ldots\right)$$

where ΔR is the instrument response (usually a thermistor voltage), c is the concentration (usually given in g/kg or g/L of solution), K is the calibration constant, M_n is the number average molecular weight, and A_2 and A_3 are "virial" coefficients. In VPO, the second "virial" coefficient, A_2, often appears to be negative for calibrants which are known to be well dissolved by the solvent employed. This indicates that there are obviously instrument and/or kinetic effects along with the thermodynamic response [1, 19]. When a new polymer type is studied for which the polymer–solvent–instrument response is not known, it is good practice to study $\Delta R/c$ over a wide range of c, up to 150 g/kg solution. Even at this high concentration, there is little A_2 contribution in the case of PIB in toluene at 50-60°C over the M_n range studied here by VPO. Polystyrene under the same conditions exhibits a significant positive A_2 ($\sim 10^{-3}$ mL mole/g^2 at 2400 molecular weight). With systematic behavior in A_2 being observed and a proper thermistor rinsing protocol, which ensures that the instrument zero is well deter-

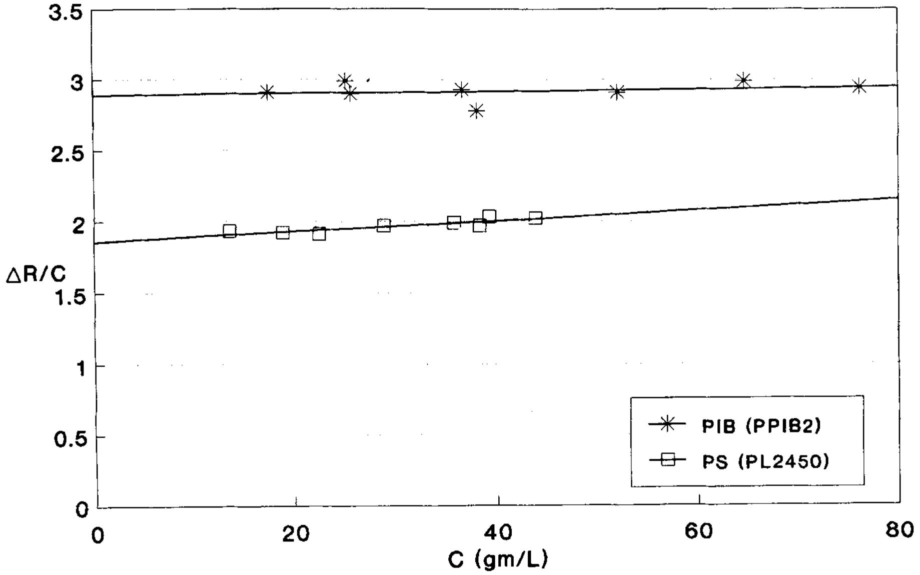

FIGURE 1 Examples of VPO data for PS and PIB. Data from Huffman Laboratories: Toluene, 60°C. The M_n value derived from the PIB data (PPIB2) is 1286, compared to 1260 ± 30 at 95% confidence limits representing the average of six measurements from three different labs (including Huffman). The M_n value derived from the PS data (PL2450) is 2410 compared to 2320 quoted by the supplier, Polymers Laboratories. The calibration constants for these two data sets are not the same, as the data were taken over two years apart.

mined, reproducible results can be obtained. Some examples of VPO data for PIB and PS from Huffman Laboratories are presented in Figure 1.

REFRACTIVE INDEX AND SPECIFIC REFRACTIVE INDEX INCREMENT

Variation with Molecular Weight

The refractive index increment (dn/dc) describes the change in refractive index of a polymer solution with respect to a change in polymer concentration. A useful approximation for dn/dc is [20]:

$$dn/dc = (n_p - n_s)/d_p \tag{1}$$

where n_p is the polymer refractive index, n_s is the solvent refractive index and d_p is the polymer density, which is also the pure polymer concentration. Equation (1) is an excellent approximation for polymers in relatively poor solvents or at low molecular weight, where the partial specific volume is essentially equal to $1/d_p$. In good solvents, a somewhat more complicated formula is required [5, 20]. It is well known that dn/dc varies with the number-average molecular weight of the polymer, [5, 6] and it is easily demonstrated that this variation is due to end-group effects. Thus dn/dc, n_p, and d_p vary nearly linearly with $1/M_n$, all approaching asymptotic limits at high molecular weight.

TABLE I

Refractive indices for polyisobutene and polystyrene (25.0°C, 589 nm)

Polymer	Sample	M_n	n_p
Polyisobutene	PIB dimer	112	1.4060
	PIB trimer	168	1.4280
	PIB tetramer	224	1.4471
	PPIB2	1260 ± 30[a]	1.4983
	PIBF2	2680 ± 80[b]	1.5039
	PIB15	35000 ± 4000[c]	1.5087
Polystyrene	PL162	162	1.4849
	PS266	266	1.5302
	PS370	370	1.5505
	PL580	550	1.5664

[a] M_n determined by VPO. Average of 6 measurements: blind duplicate measurements at three laboratories (Huffman, ARRO, and Exxon). Error estimate is 95% confidence limit.

[b] M_n determined by VPO at Huffman Laboratories. Four determinations combined into one data set with 23 concentrations. Error estimate is 95% confidence limit. Quoted M_n value for this sample, supplied by Professor R. Faust (University of Lowell), is 2500.

[c] M_n determined from LS M_w (~ 70,000) combined with SEC M_w/M_n (~ 2.0). Error estimate is a rough estimate from expected LS and SEC precision.

Though the effect of the variation of dn/dc with molecular weight on the SEC concentration detector [7, 21] and LS intensity [7, 17] is well known, there are relatively few examples of quantitative results showing the magnitude of the effects. In this section, we provide such an analysis.

We begin with a discussion of the variation of refractive index with M_n for PIB and PS. Table I displays refractive indices for the primary standards used to ascertain the M_n dependence of n_p. As described in the experimental section,

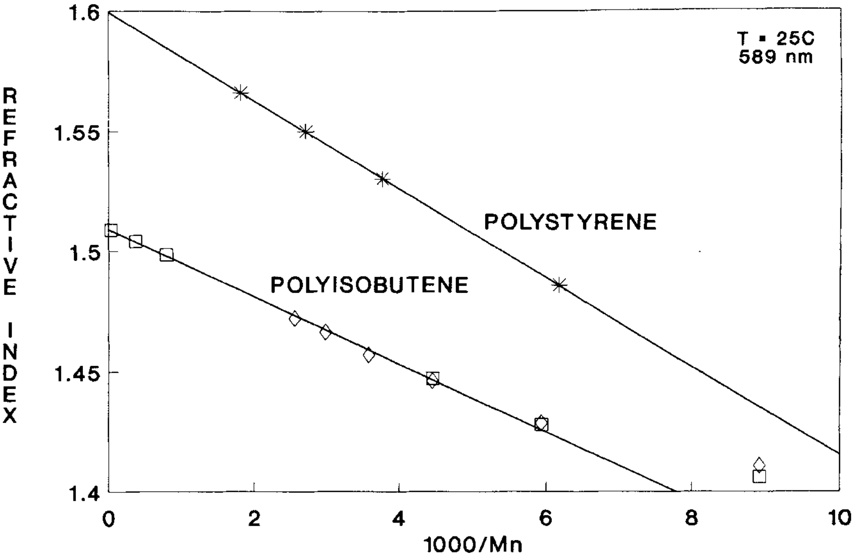

FIGURE 2 Refractive index of PS and PIB (25°C, 589 nm) versus $1000/M_n$. The squares for PIB and the asterisks for PS are current data. The diamonds are data for PIB oligomers (DP = 2–7) from Rhein and Lawson.[4] The solid lines represent least squares fits to the data; in the PIB case, the two lowest points (dimer and trimer) and the reference [4] data are excluded from the fit.

oligomers of PS and PIB were examined by GC-mass spectroscopy to confirm their molecular weights; PIB oligomers were also examined by NMR to confirm their identification as good models for oligomers of polyisobutene. The M_n values for PPIB2 and PIBF2 were determined by VPO. The M_n value for PIB15 was estimated by a combination of light scattering and SEC (see Table I). The M_n value for PL580 was assigned as 550 based on PL literature, our own SEC measurements, and published data [22]. Our PS data are restricted to the low molecular range where PS at 25°C is fluid enough to make good contact with the refractometer prism. The results are displayed in Figure 2, which includes for comparison purposes the n_p measurements of Rhein and Lawson [4] for PIB oligomers (DP = 2–7). The linear regressions of the data (excluding PIB trimer and dimer and the reference [4] data) give the following equations:

$$\text{PIB} \quad n_p = (1.5092 \pm 0.0004) - (13.9 \pm 0.2)/M_n \tag{2}$$

$$\text{PS} \quad n_p = (1.601 \pm 0.002) - (18.8 \pm 0.5)/M_n \tag{3}$$

where the error estimates correspond to 95% confidence limits. The infinite M_n limits for both PIB and PS are in reasonably good agreement with the literature [5, 23]. Because of the difficulties associated with solvent removal and achieving good optical contact for high-molecular-weight PIB samples, there is some likelihood that the true infinite M_n limit for n_p of PIB is a bit higher than the 1.5092 value, but probably no greater than 1.5095. Equations (2) and (3) may be used to calculate M_n from refractive index measurements, as suggested earlier [4]. We have tested Equation (2) on numerous occasions and are confident that M_n values

TABLE II

Refractive indices and refractive index increments for polyisobutene*

Sample	M_n	n_p	dn/dc (THF)[a]	dn/dc (heptane)[a]
Dimer	112	1.4060	[0.0050]	[0.031]
Trimer	168	1.4280	[0.0306]	[0.056]
Tetramer	224	1.4471	[0.0523]	[0.078]
Pentamer	280	1.4569[b]	[0.0638]	[0.087]
Hexamer	336	1.4665[b]	[0.0739]	[0.097]
Heptamer	392	1.4721[b]	[0.0792]	[0.103]
PIB1	470	1.4805	0.0868 [0.0878]	—
PIB2	690	1.4901	0.0961 [0.0968]	—
PIB3	810	1.4925	0.0992 [0.0990]	—
PIB4	960	1.4949	0.1013 [0.1011]	—
PIB5	1110	1.4966	0.1029 [0.1027]	0.133 [0.125]
PIB6	1300	1.4987	0.1050 [0.1045]	—
PIB7	1540	1.5003	0.1061 [0.1059]	—
PIB8	1800	1.5015	0.1075 [0.1070]	—
PIB9	2130	1.5026	0.1086 [0.1080]	—
PIB10	3300	1.5047	0.1125 [0.1098]	0.137 [0.131]
PIB11	5000	1.5058	0.1086 [0.1107]	0.138 [0.132]
PIB14	13000	1.5078	0.1122 [0.1123]	0.142 [0.134]
PIB15	35000	1.5087	0.1131 [0.1132]	0.143 [0.135]

[a] Calculated values based on n_p and d_p (see Equation 1) are shown in brackets (25°C, 589 nm).

[b] Refractive index measurements from Rhein and Lawson.[4] Original 20°C measurements adjusted to 25°C based on our determination of dn_p/dT as a function of M_n (see text).

*M_n values are those assigned based on all available data. n_p measurements at 25°C, sodium D line (589 nm). dn/dc measurements at 27°C and 633 nm. Units are mL/g

TABLE III

Refractive indices and refractive index increments for polystyrene*

Sample	M_n	n_p	dn/dc (cal)[a]	dn/dc (meas)
PL162	162	1.4849	0.093	—
PS266	266	1.5302	0.132	—
PS370	370	1.5505	0.148	—
PL580	550	1.5664	0.159	0.154
PL1700	1590	—	—	0.187
PL2450	2320	—	—	0.187

[a] Calculated dn/dc based on n_p and d_p (see Equation 1).

*n_p measurements at 589 nm; dn/dc measurements at 633 nm in THF. All measurements at 25°C. Units are mL/g.

so derived will be within the stated uncertainties in Equation (2), which correspond to about ± 150 units at 2000 M_n and about ± 3000 at 10,000 M_n. Since n_p can be measured to ± 0.0001 or better on a relative basis, errors in the m_n determination on a comparative basis would be much less.

The dn/dc values and additional n_p data are summarized in Table II for PIB and in Table III for PS. The M_n assignments for these tables derive primarily from SEC measurements to be discussed in the next section. The calculated dn/dc values are obtained from Equation (1) with the following density functions:

$$\text{PIB} \quad d_p = 0.917(1\text{–}30/M_n) \tag{4}$$

$$\text{PS} \quad d_p = 1.08(1\text{–}33/M_n) \tag{5}$$

Equation (4) is obtained from Rhein and Lawson[4] and our own internal data base on PIB densities. Equation (5) is a rough estimate based on partial specific volume measurements reported by Candau et al. [5] and the density of PL162 (0.86 g/mL). It should be noted that the dn/dc measurements in Table III are at 633 nm, while calculated values are at 589 nm. The wavelength dependence of dn/dc for optically transparent polymers is small enough [20] for this wavelength difference to be of no consequence for the present work.

Figure 3 displays dn/dc vs $1/M_n$ for PS and PIB in THF. The straightline fits correspond to the equations:

$$\text{PIB} \quad dn/dc = 0.115(1\text{–}122/M_n) \tag{6}$$

$$\text{PS} \quad dn/dc = 0.190(1\text{–}83/M_n) \tag{7}$$

where the slopes ($S = 122$ and $S = 83$) provide the correction factors necessary to correct the SEC DRI signal and LS data for polydisperse samples. We, and others, [24] here determined S for PS and PIB from SEC experiments (integrated signal area/c vs. $1/M_n$) obtaining identical S values (within $\pm 2\%$). Since the DRI detector in our SEC instrument operates at 1000 nm, these results confirm the expected lack of any significant wavelength dependence for S. Taking into account all results available to us for PIB, we use $S = 120$ in analysis of SEC data to follow. For polymethylmethacrylate (PMMA) in THF, we find $S \cong 90\text{–}100$, based on n_p and d_p data from Sanayei [25]. As others have shown, [5, 26] dn/dc can be calculated very accurately from specific refractions [27] if the M_n dependence of

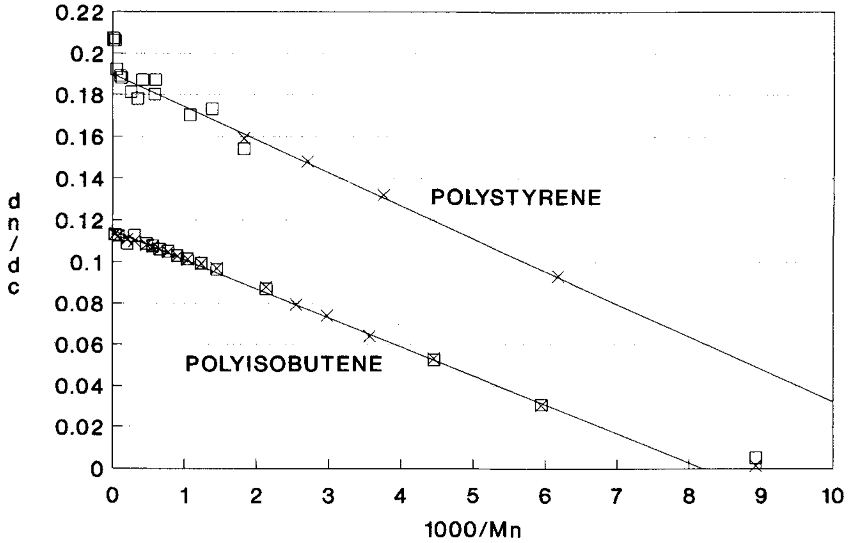

FIGURE 3 *dn/dc* in mL/g for PS and PIB in THF solvent versus $1000/M_n$. The squares represent measured *dn/dc* values at 27°C and 633 nm. The *X*'s represent calculated *dn/dc* values from Equation (1), 25°C and 589 nm. PIB data are taken from Table II. PS data are taken from Table III, except for some of the high-molecular-weight data, which are unpublished results from earlier studies by N. Hadjichristidis. The lines represent best fits to the data, excluding the highest molecular weights for PS and the dimer for PIB. The upward curvature in the PS data at high molecular weight is real and probably due to a decrease in specific volume.[5]

d_p (or, more precisely, partial specific volume) is known. This approach yields near quantitative agreement with our data for PIB in THF and heptane, though in the heptane case, the partial specific volume of PIB in heptane (e.g., ~ $0.97/d_p$ at 2000 M_n) must be explicitly taken into account [20].

For the PS case, it is important to note that Equations (3), (5), and (7) refer specifically to PS with an *n*-butyl group at one end of the polymer, the most common material available from suppliers of PS standards. For DP = 1, this PS structure is about 30% "alkane." For low-DP PS, all physical properties are expected to be sensitive to the chemical identity of this end group. For example, if *n*-butyl is replaced by a proton (material supplied to us by PSS), our preliminary result for *S* in Equation (7) is 50, compared to 83 for the *n*-butyl case. SEC calibration curves for these two PS structures are also significantly different in the low DP range (DP < 9). End-group effects are much less important for PIB. Although there are a variety of end group structures in PIB prepared by conventional cationic polymerization, they differ principally in the position of the double bond (which is always at or near the chain end) [14]. The specific refractions $[(n^2 - 1)/(n^2 + 2)d]$ of, for example, oligomers of butene with different olefin structures would be expected to be essentially the same, since the principle of bond additivity of specific refractions works extremely well for non-conjugated organic materials [27]. The same would be true for copolymers of isobutene and *n*-butene and for poly(*n*-butene). If specific refractions are invariant, *dn/dc* will be essentially invariant [20]; *n* and *d* data for model dimers support this conclusion [18]. Therefore, the M_n dependence of *dn/dc*, *S* in Equation (6), is expected to be

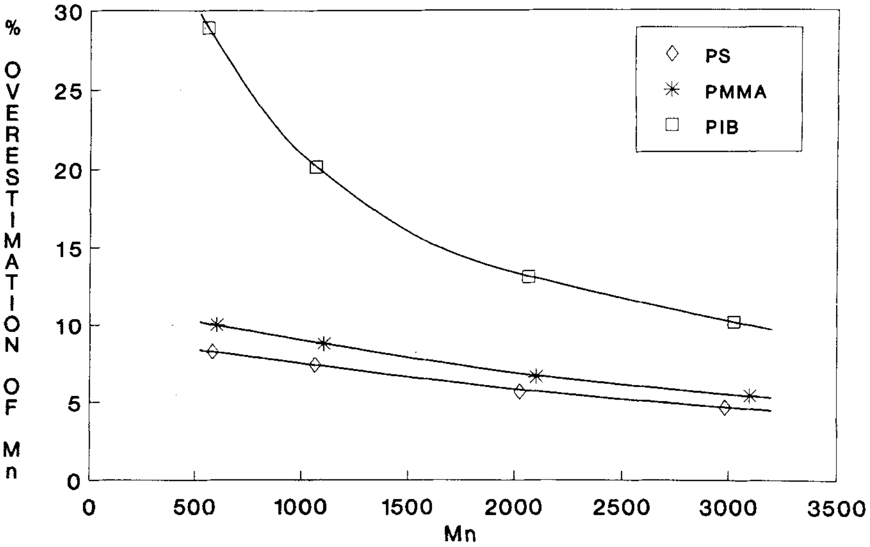

FIGURE 4 Simulation of SEC experiment (THF, 30°C) for most probable distribution (monomer removed). Results are shown for calculations of the percent overestimation of M_n if corrections for the refractive index variation with M_n are ignored. Correction factors for PS, PIB, and PMMA are given in the text.

independent of the specific end group structure for PIB. As an extreme example, we find $S \sim 110$ for poly(1-butene) which is very similar to the $S = 120$ result for PIB; in fact, even this small difference is entirely attributable to lower density (and, therefore, lower n_p) of poly(1-butene) at high-molecular-weight (0.87 compared to 0.917 g/mL for PIB). Also, as already noted, SEC retention times for PIB oligomers are essentially unaffected by the small quantities of copolymerized 1-butene present in commercial PIB samples (as exemplified by oligomers resolved in SEC analysis of APS6K and PPIB2).

Consequences of *dn / dc* Variation with Molecular Weight in SEC and LS

The differential refractometer detector on the SEC instrument measures the difference in refractive index between the eluting polymer solution and the THF solvent. SEC data are corrected for the *dn/dc* variation by dividing the observed DRI signal by *dn/dc* or, since only relative concentrations are required, by $(1 - S/M)$, where M is the molecular weight of the SEC slice [21]. We refer to this process as the "RI correction." To illustrate the effect of the RI correction on SEC, we have conducted model calculations using the most probable $(M_w/M_n = 2)$ molecular weight distribution (with monomer removed). To simulate an "uncorrected" SEC distribution, we multiply our model distribution by $1 - S/M$. We then calculate and compare molecular-weight averages, with and without the RI correction. We consider three cases corresponding approximately to PIB, PS (S = 80), and PMMA (S = 90) in THF. For PIB we have used a cubic fit to the *dn/dc* data so that the calculations can be extended all the way to dimer $[dn/dc = 0.115(1-133/M_n + 315000/M_n^3)]$. Results are shown in Figure 4. At 1000 M_n, failure to perform the RI correction results in overestimations of M_n by

TABLE IV

Effect of refractive index correction on M_n and M_w determinations for polydisperse PIB APS6K in THF

	Supplier M	Corrected	Uncorrected	Percent Overestimation[a]
M_n-SEC	2060	2140	2470	15.4
M_w-SEC	5900	6190	6420	3.7
M_w-LS[b]	5900	6190	6690	8.0

[a] Percent overestimation comparing uncorrected versus corrected values.

[b] Assumes THF solvent and that the dn/dc measured for this polydisperse sample is used in LS calculation of M_w. Uncorrected value is calculated from Equation (8).

20%, 8%, and 9%, respectively for PIB, PS, and PMMA; at 2000 M_n, the overestimations are 13%, 6%, and 7%. Thus, RI corrections for SEC measurements of M_n can be quite significant. Corrections for M_w are significantly less. Our RI corrections for PS M_n are about twice as large as those found by Sanayei and O'Driscoll [12] in similar model calculations; they found results equivalent to S = 38 for PS in THF, which is more than a factor of two lower than our result [24]. Support for our PS results can be found in the work of Barrall et al. [7] who studied PS in toluene and the effect of RI variation on SEC and LS. The RI correction for PS in toluene is greater than that for PS in THF since n_s for toluene is greater than n_s for THF (1.4980 vs. 1.4050 at 25°C, but still below n_p of PS for DP > 1). The dn/dc measurements of Barrall et al. yield $S \sim 170$ for PS in toluene (see also reference 5), which is in close agreement with the value calculated from Equations (1), (3), and (5) (also $S \sim 170$). Barrall et al. find a 13% overestimation of M_n in SEC analysis of a PS sample in toluene with $M_n = 5400$ and $M_w/M_n \sim 2$. For this same sample in THF, we would expect a correction of only a few percent.

Results for an available polydisperse PIB standard, APS6K, are shown in Table IV. APS6K is a polydisperse PIB with $M_w/M_n \sim 3$, supplied as an SEC standard by American Polymer Standards. This example should be a good representation of the expected result for commercial PIB samples, since APS6K is obtained by APS from a commercial source. Here and elsewhere in the analysis of SEC experimental data for PIB, we use $S = 120$ since our polydisperse samples contain no detectable dimer, and little or no trimer. Without an RI correction, M_n, for APS6K is overestimated by 15.4% and M_w is overestimated by 3.7%. The 15.4% correction for M_n is a bit larger than the 13% value for $M_n = 2000$ in Figure 4, as expected since APS6K has a polydispersity of almost 3 compared to about 2 for the Figure 4 calculations. We also include in the table an estimate of the overestimation of M_w from light scattering if the RI variation is ignored. The 8% error in LS can be derived from the equation [17]:

$$M_w^{\text{obs}} = M_n + \left(M_w^{\text{true}} - M_n\right)/\left(1 - S/M_n\right)^2 \tag{8}$$

This formula assumes that the dn/dc measured for the polydisperse sample is used in the M_w^{obs} calculation from LS data. Equation (8) has been used to correct all our light-scattering data; the S value for heptane (our LS solvent) is 108 from analysis of the Table II data.

Temperature Effects

The temperature dependence of dn/dc is expected to be small [20]. Nevertheless, we have evaluated the temperature dependence of dn/dc of PIB over a broad M_n range in order to ensure that the modest difference in the temperature chosen for SEC measurements (32°C vs. 25°C for n_p and 27°C for dn/dc) does not have any effect on the size of the RI correction. We have determined the temperature dependence of n_p over the range 15–60°C and over the M_n range 112–35,000: $dn_p/dT = -3.0 \times 10^{-4}(1 + 73/M_n)°C^{-1}$. Our result for the temperature dependence of the PIB density is -5.5×10^{-4} g/mL °C, essentially independent of M_n over the M_n range measured (300–2500). For THF dn_s/dT is $-4.4 \times 10^{-4}°C^{-1}$ with $n_s = 1.405$ at 25°C. If these values are substituted into Equation (1), we find $d(dn/dc)/dT \cong 2 \times 10^{-4}$ mL/g °C for PIB at high M_n and approaches zero for PIB trimer. The temperature dependence of S ($dS/dT = -0.030$ g/mol °C) is completely negligible for our purposes. We have not evaluated $d(dn/dc)/dt$ or dS/dT for PS, but expect the same conclusions.

Intrinsic Viscosities, Hydrodynamic Radii, Radii of Gyration, and “Universal” SEC Calibration

Universal calibration (UC) in SEC [1–3, 15, 16, 28] is based on the premise that polymers with the same size will elute at the same retention volume, and further that this size may be approximated by the hydrodynamic volume, V_h. V_h is proportional to $[\eta]M$, and for convenience, we define: $V_h = [\eta]M$ with $[\eta]$ given in dL/g. At high molecular weights for flexible polymers, this premise is supported by a great deal of experimental data, [1–3, 29] although failures have been noted for rod-like polymers [30]. Although UC has been applied at low molecular weights (< 1000), [12, 31] the theoretical and experimental justification for the extension to low molecular weight is weak[1–3, 10]. In this section, we examine this question quantitatively. We begin with establishment of the molecular weight and intrinsic viscosity database for PIB, PS, and alkanes in THF. We then present SEC data and test UC as well as other [29] approaches to“universal” calibration.

We have expended significant effort in determining the correct intrinsic viscosity molecular weight relationships for these polymers in THF. Data for PIB and PS are summarized in Tables V and VI and Figures 5–7. Table V displays $[\eta]$ data for PIB along with most of our M_n and M_w database for the various PIB samples employed in this work (see experimental section for a description of the PIB samples). All data in this table derive from the present work, except as noted in footnote g. M_p values are shown in Table V for the samples to be used later for SEC calibration and testing of UC. These M_p assignments are based on all data shown, $[\eta]$ data in benzene and heptane for selected samples (not shown), and information provided by suppliers [32]. Except as indicated in footnotes of Table V, our $[\eta]$ data for THF, heptane, and benzene are completely consistent with the literature [11, 33, 34]. Our M_p assignments were tested via SEC for essentially all of the samples shown in the table. From Table V we have taken only data for narrow standards ($M_w/M_n \leq 1.4$) for inclusion in Figures 5 and 6, since corrections to M_v would be necessary for the broad standards. Application of appropriate corrections for the broad standards places these data on a common line with the narrow standard data shown in Figure 6.

TABLE V

Polyisobutene: molecular weights, intrinsic viscosities, polydispersities and radii of gyration*

Sample	M_n	M_w	[η] dL/g (30C THF)	M_p (Assigned)	M_w/M_n (SEC)	M_w (Assigned)	R_g (Å)[h]
Dimer	112[a]	—	0.0036	112	1.00	112	1.69
Trimer	168[a]	—	0.009	168	1.01	168	2.30
Tetramer	224[a]	—	0.014	224	1.01	224	2.86
PIB1	475[b]	—	0.024	—	1.19	560	—
PIB2	730[b]	—	0.030	700[c]	1.16	790	6.32
PIB3	830[b]	—	0.032	—	1.18	940	—
PIB4	970[b]	—	0.035	—	1.21	1160	—
PIB5	1100[b]	1400[d]	0.039	—	1.18	1310	—
PIB6	1320[b]	—	0.041	—	1.20	1520	—
PIB7	1560[b]	—	0.045	—	1.17	1780	—
PIB8	1810[b]	—	0.048	—	1.15	2050	—
PIB9	2110[b]	—	—	—	1.15	2520	—
PIB10	3100[b]	4300[d]	0.070	—	1.30	4300	—
PIB11	—	7200[d]	0.087	—	1.23	6600	—
PIB12	—	6400[e]	—	—	1.21	6600	24.4[25.1]
PIB13	—	9700[e]	—	—	1.20	9800	29.7[29.8]
PIB14	—	58000[d]	0.30	—	4.10	60000	—
PIB15	28000[b]	65000[d], 80000[e]	0.36	—	2.00	70000	—
PIBF1	2300[b]	3000[d]	—	—	1.23	2900	15.2[14.7]
PSS616	530[b], 570[f]	—	0.026	616[c]	1.10	650	5.9
PSS1K	1050[b], 1030[f]	—	0.037	1120	1.06	1170	8.9
PSS2K	1830[b], 2000[f]	—	0.052	1850	1.16	2300	12.0
PSS4K	2630[b], 2800[f]	4100[d]	0.070	4100	1.40	4300	18.6
PSS10K	—	8700[d]	0.110	9200	1.21	9600	29.0
PSS20K	—	18000[d]	0.189	19600	1.16	23000	42.5
PSS71K	—	—	0.39	71000	1.17	66000	81.0
PSS86K	—	—	0.47	87600[g]	1.15	86000[g]	—
PSS108K	—	—	0.58	108000[g]	1.13	112000[g]	—
APS160K	—	—	0.61	—	1.21	160000[g]	—
APS247K	—	—	0.87	—	1.20	247000[g]	—
APS300	310[b]	—	0.019	—	1.16	360	—
APS6K	2080[b]	—	0.082[i]	—	2.90	6190	—
PPIB1	1780[b]	—	0.068	—	2.50	4300	—
PPIB2	1275[b], 1260[j]	2600[d]	0.054	—	2.00	2600	—

[a] Confirmed by GC mass spectroscopy.

[b] M_n determined from measured refractive index and Equation (2).

[c] M_p assigned based on resolved oligomer peaks. For PIB2 case, the assignment is about half way between DP = 12 (M = 672) and DP = 13 (M = 728) because of the nearly equal signals for these two peaks (Figure 9).

[d] LALLS, heptane, 27°C.

[e] Light scattering—Zimm analysis,heptane, 27°C.

[f] VPO determination of M_n, 50°C, toluene solvent, 3-4 concentrations. PSS quotes 3100 by VPO for PSS4K.

[g] M_w and M_p values for these four standards are from the suppliers (Polymer Standards Service and American Polymer Standards). They are fairly consistent with our THF and benzene [η] data and published [η]-M relationships for these solvents (references 11, 33, and 34), which suggest M_w values of 95K, 120K, 145K, and 250K.

[h] Interpolated, based on M_p, from de Bolt RIS results (reference 47) which were available for integer degrees of polymerization. Values in brackets for three samples originate from SANS measurements in deuterated decane (this study).

[i] This sample gave identical results in the Viscotek and suspended-level viscometers.

[j] VPO—See Table I.

*All data are from present work. Our M_p and M_w assignments are based on all available data. SEC M_w/M_n values are from SEC calibration based on M_p values shown.

TABLE VI

Polystyrene: molecular weights, polydispersities, intrinsic viscosities, and radii of gyration*

Sample	M_w	M_w/M_n	M_p	$[\eta]$(dL/g)[c]	Rg(Å)[d]
PL162	162	1.0	162	0.0117	—
PS266[a]	266	1.0	266	0.0181	—
PS370[a]	370	1.0	370	0.0219	—
PS474[a]	474	1.0	474	0.0238	—
PL580	650	1.16	580	0.0265	4.75
PL980	1020	1.09	980	0.0305	—
PL1320	1300	1.07	1320	0.0341	8.05
PL1700[b]	1670	1.06	1700	0.0388	9.55
PL2450[b]	2410	1.05	2450	0.0457 (0.044)	12.4
PL2950	2970	1.05	2950	0.0497	13.5
PL3250[b]	3210	1.04	3250	0.0527	14.4
PL5K	5000	1.05	5050	0.0647	18.6
PL7K	7100	1.04	7000	0.0772	22.5
PL10K	9900	1.03	10100	0.0937 (0.093)	27.4
PL12K	11700	1.03	11600	0.1033	29.6
PL22K	22100	1.03	22000	0.155	41.0
PL29K	28600	1.03	28500	0.180	47.0
PL30K	30200	1.03	30300	0.193	49.0
PL52K	51000	1.03	52000	0.275	—
PL66K	66000	1.03	66000	0.332	73.0
PL96K	94000	1.04	96000	0.433	—
NBS706	276000	—	—	0.88 (0.88)[e]	—

[a] These samples were prepared as fractions from PL580. PSS also supplies PS266 and PS370, which were identical to our fractions. Remaining samples, except for NBS706, are from Polymer Laboratories (PL); PL M_w/M_n values shown in the third column are in excellent agreement with our own results (not shown).

[b] VPO data were obtained from Huffman Laboratories on these three samples; results are: 1710, 2410, and 3070 in good agreement with quoted VPO values from PL (1630, 2430, and 3200).

[c] THF at 30°C. This study, Viscotek, except for values shown in parentheses for three samples, which were obtained on suspended-level viscometer.

[d] Values interpolated, based on M_p, from experimental results of Einaga et al.,[8] no experimental R_g data available below $M = 580$.

[e] Literature values for $[\eta]$ of NBS706 range from 0.86 to 0.94. Our Viscotek instrument was calibrated to the 0.88 value shown, which was obtained from the present work on a suspended-level viscometer.

* Molecular weight data are from supplier (Polymer Laboratories), except as noted; $[\eta]$ and R_g data from present work.

PS data for $[\eta]$ in THF are shown in Table VI and Figure 7. For polystyrene, narrow standards are available from numerous suppliers. We have performed SEC measurements on PS standards from many suppliers and have determined those from Polymer Laboratories (PL) to be the most internally consistent and to represent a reasonable average of the complete sample population studied [35]. We used PL-assigned molecular weights for PS, after checking their M_n assignments for three samples by VPO measurements (see Table VI).

For PIB in THF, the data of Figure 5 indicate that a Mark-Houwink relationship with a slope of 0.50 can be used for $600 < M_w < 10{,}000$. Even though THF is a moderately good solvent for PIB, Figure 5 shows that at sufficiently low molecular weight the excluded volume effect vanishes, and the expected 0.5 slope consistent with unperturbed dimensions is observed. For PIB in benzene, a theta solvent at 25°C, and in isoamyl isovalerate (IAIV), also a theta solvent at 25°C, a slope of 0.5 is maintained [33] up to at least $M_w = 10^6$ (Figure 5), whereas the THF data show a higher slope above about $M_w = 10^4$ as shown in Figure 6 and the work of

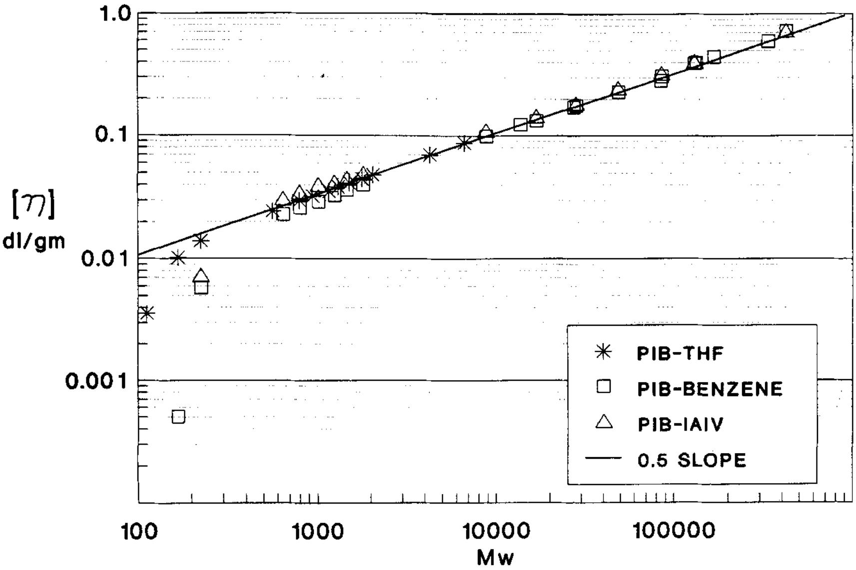

FIGURE 5 Intrinsic viscosity of PIB in THF (30°C), benzene (25°C) and IAIV (25°C) vs. M_w. The THF data are from the present work (suspended-level viscometer); the remaining data are from reference 11. The 0.5 slope line corresponds to: $[\eta] = 0.00107\, M_w^{0.5}$ dL/g.

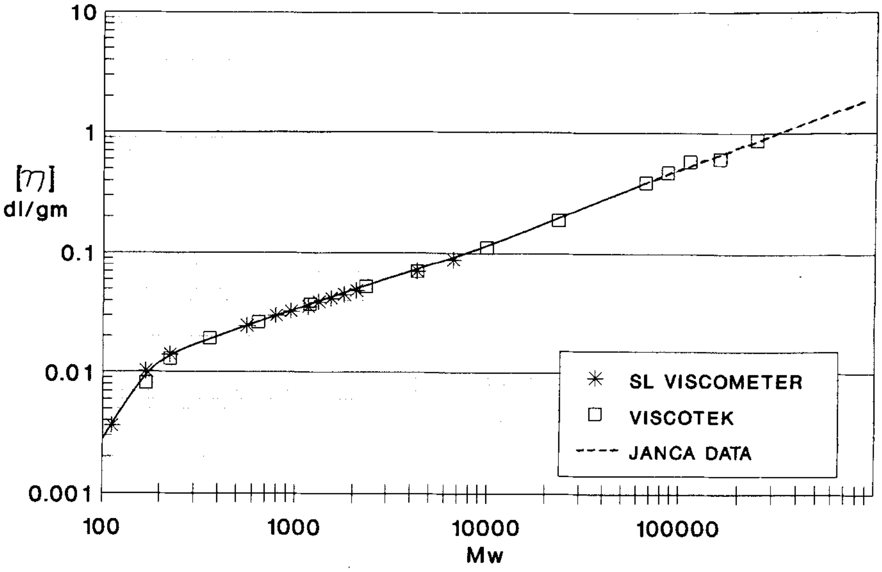

FIGURE 6 Intrinsic viscosity of PIB in THF (30°C) vs. M_w. All data are from present work (asterisks, suspended-level viscometer; squares, Viscotek online viscometer), except for the dashed line at high molecular weight representing data from reference 34.

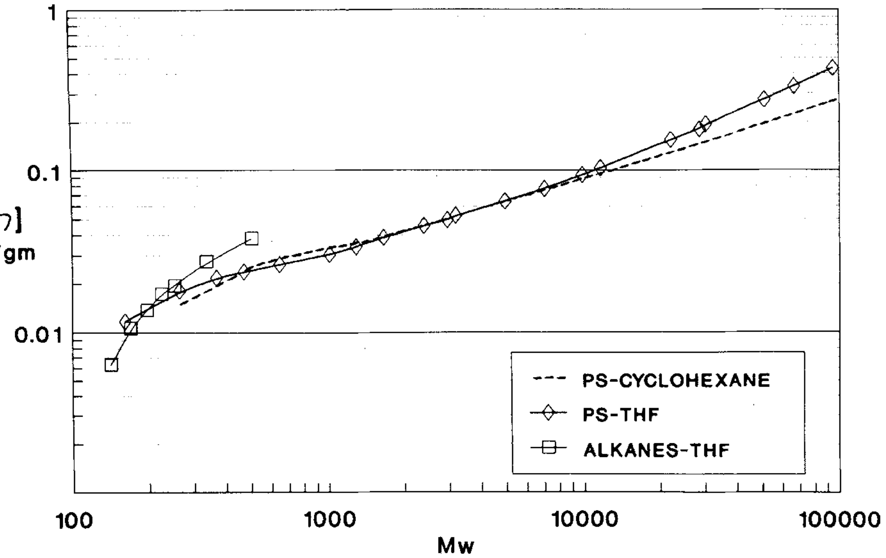

FIGURE 7 Intrinsic viscosity of PS in THF (30°C), PS in cyclohexane (34.5°C), and *n*-alkanes in THF (30°C) versus M_w. All data from present work with Viscotek viscometer, except PS cyclohexane data, which are taken from reference 8.

reference [34]. Below about $M_w = 2{,}000$ the benzene data fall below the 0.5 line, whereas in IAIV there is first a positive deviation to less than a 0.5 slope and then a divergence to low $[\eta]$ values with a steep slope below about $M_w = 500$. For PIB in THF a number of factors seem to cancel yielding a 0.5 slope down to below $M_w \sim 600$ at which point $[\eta]$ diverges to low values with a steep slope. Our complete data set for narrow molecular weight distribution PIB in THF is shown in Figure 6. Note that our data smoothly merge into that of reference [34] and that data from the Viscotek and the suspended-level viscometers form a common curve.

PS$[\eta]$ data are presented in Figure 7 for two solvents, although much more are available in the literature. In THF, our SEC solvent, there is an inflexion in the viscosity molecular weight behavior, unlike the PIB case. In fact, there is almost no region where a 0.5 slope is observed. Above $M_w \sim 2000$ the slope is above 0.5, for $500 < M_w < 1200$ it is below 0.5 and then it falls off with a higher slope again at very low M. Cyclohexane at 34.5°C is a theta solvent yielding a 0.5 slope above $M_w \sim 2000$. At low M_w, cyclohexane data behave qualitatively like THF data but with a somewhat different pattern of inflexion. To represent any of this data with a single Mark-Houwink relationship, or one of the form $[\eta] = KM^{1/2} + K'M$, [36] is not possible over any significant region in M which includes this low-molecular-weight range. Our data for PS in THF are in excellent agreement with those of Armonas[37].

It is not our intent here to explain this complex behavior of PS. Einaga et al. [8] recognize that there are specific solvent effects on unperturbed dimensions and furthermore that even in theta solvents there are stiffness effects that cause the inflexion to higher $[\eta]$ and a flatter slope as one proceeds to low molecular weight. This can be explained by the helical wormlike chain model in the context of proper hydrodynamic interaction calculations [8]. At very low molecular weight, $[\eta]$ departs toward negative values due to packing effects. Abe et al. [11] simply correct

TABLE VII

n-alkanes: molecular weights, intrinsic viscosities, and radii of gyration

Number of Carbons	M^a	$[\eta]$ (dL/g)[b]	R_g (Å)[c]
10	142	0.0063	3.15
12	170	0.0106	3.62
14	198	0.0137	4.10
16	226	0.0173	4.10
18	254	0.0195	5.05
24	338	0.0275	6.34
36	506	0.0381	8.50

[a] These samples are monodisperse.

[b] THF at 30°C, this study.

[c] Personal communication from Tonelli: data at 30°C.

empirically for the packing effect deviations and do not attempt to model the behavior.

Intrinsic viscosity data for *n*-alkanes are shown in Table VII. *n*-Alkanes are soluble up to about C_{36} in THF at 30°C. In this low-molecular-weight range, pure compounds are available, and there is no doubt about molecular weights. The intrinsic viscosities reported in Table VII (and included in Figure 7) are consistent with the literature [38] and have been collected with the same Viscotek calibration as our PIB and PS data above.

To summarize the preceding discussion of $[\eta]$, we believe our $[\eta]$ data have an absolute uncertainty of $\leq 5\%$ and a relative uncertainty $\leq 2\%$ over the molecular-weight range 300–100,000 based on the consistency of SEC and $[\eta]$–M analyses. For the lowest oligomers ($M < 300$), uncertainties are somewhat higher, as the viscometer signal is lower and there is no basis for assuming a form for the $[\eta]$–M relationship. Uncertainties in M_p assignments range from essentially 0% in the oligomer range to about $\pm 5\%$ for $M_p < 10^4$ based on internal consistency of our LS, VPO, SEC, n_p, and $[\eta]$ database. In the high-molecular-weight range ($\sim$ 50,000), we have expended less effort in confirming M_p values given by suppliers but believe the values we have used are accurate to at least $\pm 10\%$ (see footnote g in Table V).

SEC data for PS and PIB taken on the High Resolution column set are displayed in Figures 8 and 9. The PS data allow determination of peak retention times for DP = 1 to 9 (M_p = 162–994). The PIB data allow determination of peak retention times for DP = 2–14 (M_p = 112–784). The use of authentic oligomers for PS and PIB leaves no doubt as to the correctness of these M_p assignments. The smooth progression of SEC retention times, to be discussed shortly, provides further confirmation. The PIB fraction (PIB2) data in Figure 9 were subjected to a log-normal (essentially Gaussian, since skewing was minimal) deconvolution routine, which confirmed our process for extraction of peak retention times and demonstrated that the curve shape can be reproduced with the assumption that the only species present are distinct oligomers. On the Linear column set, PS and PIB oligomers are resolved up to DP of about 5 and 4, respectively.

Combining the M_p-retention time data from Figures 8 and 9 with M_p and peak retention time measurements for the PS samples in Table VI and a subset of the PIB samples in Table V (those with M_p assignments), we have constructed the

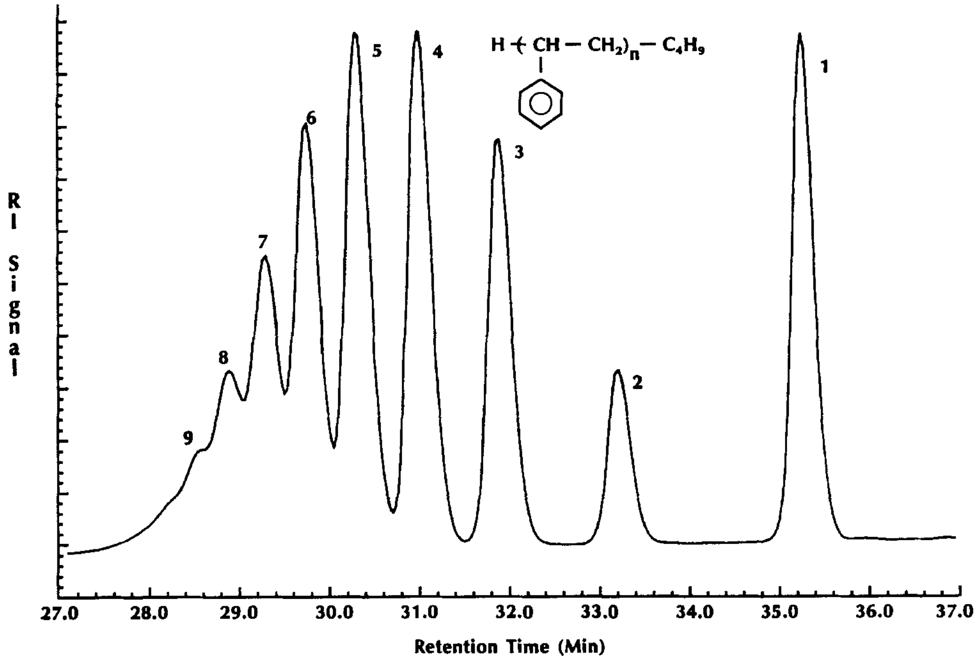

FIGURE 8 SEC chromatograms for PS in low-molecular-weight region taken on High Resolution Column set (THF, 32°C). The sample is a mixture of PL162 (DP = 1) and PL580. DP assignments for the first 9 peaks are indicated. These PS samples have *n*-butyl end groups.

SEC calibration curves shown in the upper portions of Figure 10 for the High Resolution columns and Figure 11 for the Linear columns. (The Linear calibration curve in Figure 11 produced the SEC results for APS6K given in Table IV.) Similarly obtained calibration curves for alkanes are also shown in the figures. We have included only a subset of Table V data for PIB in these analyses for two reasons: 1) we wanted, to the extent possible, to base this work on polymer standards that are commercially available; and 2) supplies of most of the remaining standards were essentially exhausted at this phase of work. Over the M_p range 200 to about 15,000, the PS and PIB calibration curves are almost perfectly parallel for both column sets, with both sets yielding $M_p^{\mathrm{PS}}/M_p^{\mathrm{PIB}} = 1.20 \pm 0.02$. This is a very convenient and useful result. At high molecular weight, $M_p^{\mathrm{PS}}/M_p^{\mathrm{PIB}}$ decreases and begins to approach 1.0 at $M_p \sim 100{,}000$. At M somewhat above 100,000 (not shown in the figures), $M_p^{\mathrm{PS}}/M_p^{\mathrm{PIB}}$ becomes less than one because THF is a better solvent for PS than PIB and excluded volume effects eventually make PS coil sizes larger than those for PIB at a given molecular weight. Alkane data do not parallel PS and PIB data; the relationship we find between M_p^{PS} and M_p for *n*-alkanes is in quantitative agreement with published data of Mori and Yamakawa [39].

Shown in the lower portions of Figures 10 and 11 are UC curves, V_h ($\equiv [\eta]M_p$) vs. retention time, for PS, PIB, and alkanes. All $[\eta]$ values and M_p values used in constructing these UC curves are given in Tables V–VII, except for PIB oligomers with DP = 5 to 14, where the $[\eta]$ values are derived by interpolation of the data in Figure 6. Results for the two column sets are in excellent agreement. Though PIB and alkane data come reasonably close to sharing a common "universal" curve, the

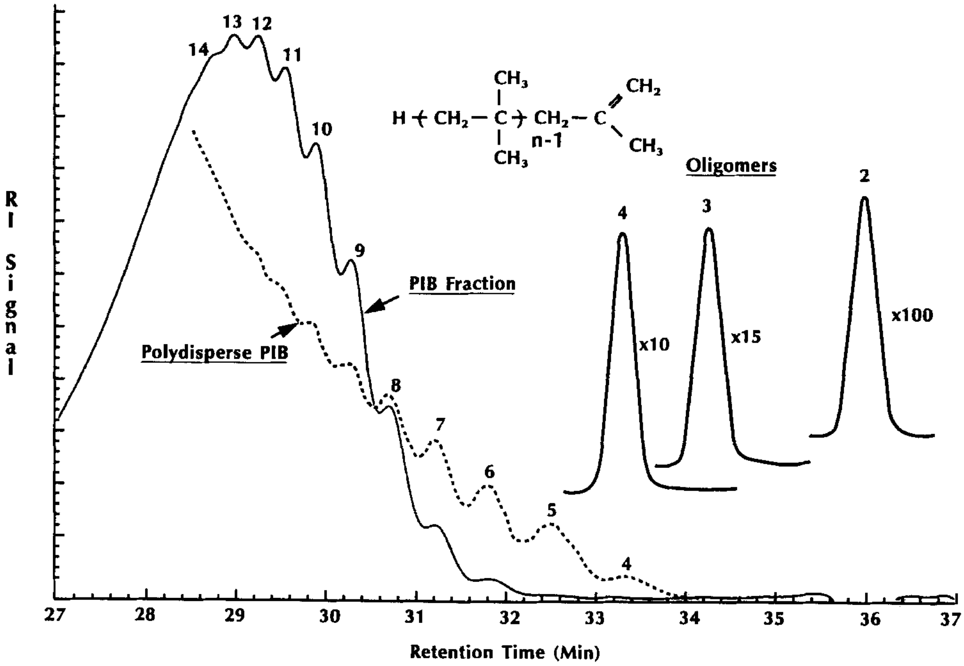

FIGURE 9 SEC chromatograms for PIB in the low-molecular-weight region taken on the High Resolution Column set (THF, 32°C). The samples are pure oligomers (DP = 2, 3, 4), polydisperse PIB (sample PPIB1), and a PIB fraction derived from PPIB1 (PIB2). See Tables II and V for more detailed descriptions of these materials. DP assignments are shown for DP = 2 to 14. The multipliers indicated for the DP = 2–4 oligomers are the intensity factors required to adjust the RI signals for these materials to the same scale as the polydisperse PIB.

PS data differ dramatically in the low-molecular-weight region. Only above $M_p \sim 5000$ can it be stated with any certainty that the UC concept is valid. Below $M_p = 1000$, UC is clearly not valid. These results contradict the conclusions from previous work in toluene,[10] where PS and *n*-alkanes were compared graphically on multi-decade logarithmic plots; numerical comparisons were not reported. Significant errors can look small on multi-decade logarithmic plots. We have much more extensive data than reference 10 and believe we would reach the same conclusions for toluene as we have for THF.

The entire process of generating the SEC data for construction of Figures 10 and 11 was repeated after a two-month interval; the results were indistinguishable from those displayed in Figures 10 and 11. The Linear calibration from the second set of experiments yielded $M_n = 2150$ and $M_w = 6120$ for APS6K compared to 2140 and 6190 from the first set (see Table IV). Similar comparisons of other polydisperse samples suggest a repeatability of about $\pm 2\%$ for M_n determinations in this SEC calibration process.

To explore whether or not the butyl end group on our PS samples had any effect on the failure of UC, we obtained two samples of PS with protons at each chain end from PSS (designated H-PS). These samples had Mn's of 540 and 820, each with Mw/Mn = 1.16. Ethylbenzene (DP = 1 for H-PS) was used to confirm oligomeric assignments and in the construction of the H-PS UC curve. The

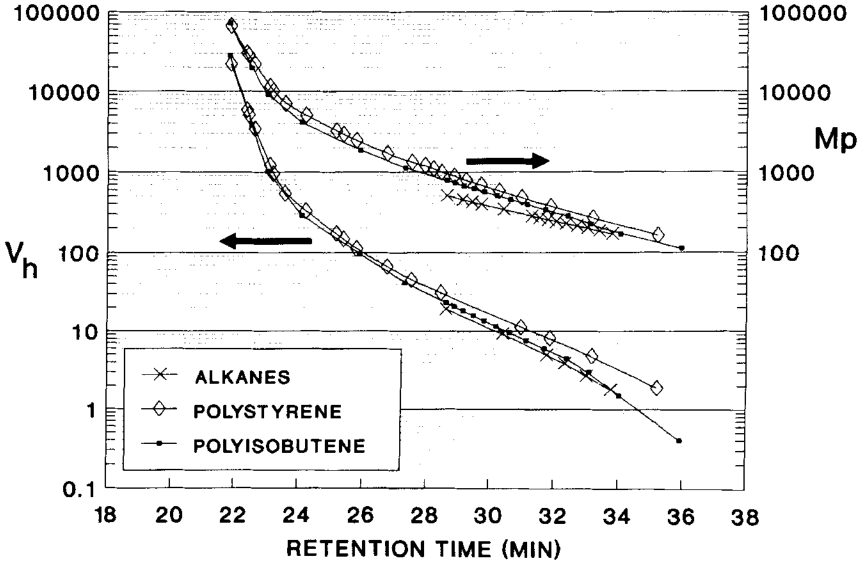

FIGURE 10 SEC calibration curves (M_p versus retention time, upper set of curves) and universal calibration curves ($V_h \equiv [\eta]M_p$ vs. retention time, lower set of curves) for PS, PIB, and alkanes on High Resolution columns (THF, 32°C). Retention times and M_p values for low-molecular-weight region (DP = 2 to 14 for PIB and DP = 1 to 9 for PS) are obtained from SEC chromatograms such as those shown in Figures 8 and 9. Alkane data are obtained in a similar manner. For the remaining data, peak retention times are determined in the conventional manner and combined with M_p assignments given in Tables V–VII. V_h values are calculated from $[\eta]$ and M_p values given in the same tables, with the exception of $[\eta]$ values for some of PIB oligomers (DP = 5–14), which are interpolated from Figure 6. Lines drawn through each data set are guides for the eye, not analytical fits to the data.

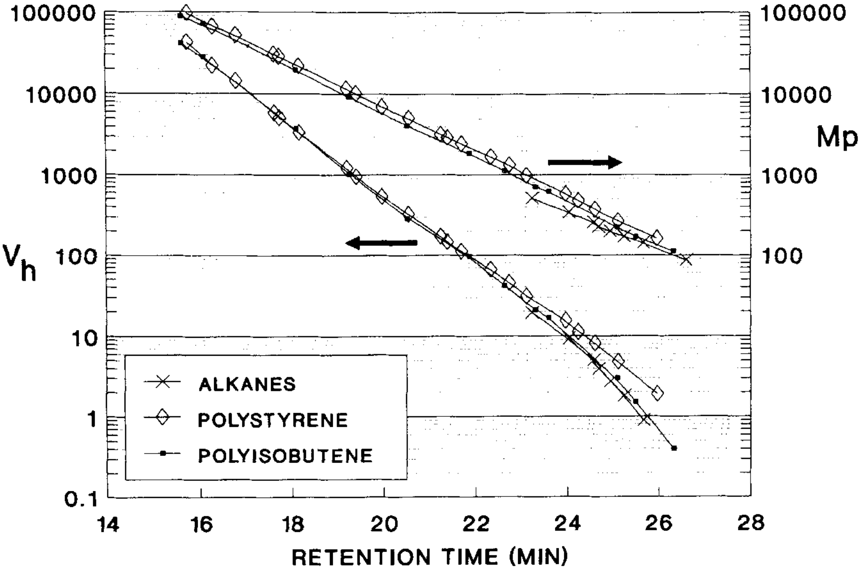

FIGURE 11 SEC calibration curves (M_p vs. retention time, upper set of curves) and universal calibration curves ($V_h \equiv [\eta]M_p$ versus retention time, lower set of curves) for PS, PIB, and alkanes on Linear columns (THF, 32°C). Peak retention times are determined in the conventional manner and combined with M_p assignments given in Tables V–VII. V_h values are calculated from $[\eta]$ and M_p values given in the same tables. Lines through each data set are guides for the eye.

disparity between UC curves for H-PS and PIB was significantly larger than that displayed in Figures 10 and 11. Even H-PS and butyl-PS do not share a common UC curve at low molecular weight.

In order to eliminate factors associated with specifics of SEC column manufacture as a source of the breakdown in UC, we explored a comparable five-column set from Waters Associates (Micro Styrogel, 2 × 100 Å, 1 × 500 Å, 1 × 10^3 Å, and 1 × 10^4 Å, all 7.8 × 300 mm). The results were essentially identical to those displayed in Figures 10 and 11 for the two PL column sets.

We note in passing that similarly obtained data for PMMA, which we will not present here, show universal behavior in comparison to PS from 1000–100,000 in agreement with other workers [12, 40]. In our results, there is some hint of departure from UC below 1000, which could not be confirmed because authentic oligomers of PMMA were not available to us.

Molar volumes [10, 41, 42] and "mean projection lengths" [1, 29] have also been used as measures of SEC separation at low molecular weights. Although it has been shown [42] that these approaches do not lead to universal behavior, we will briefly summarize results from a molar volume analysis of our data. Postulating elution at equal molar volume relates M of PS, PIB, and n-alkanes accurately within ±8% in the 100–200 molecular-weight region. Above that range, it fails for the n-alkane–PS comparison. At a PS M of 890, the predicted alkane M is 700, and the actual alkane M is 475, a 50% overestimate. However, perhaps by accident, a ratio of $M_{\mathrm{PS}}/M_{\mathrm{PIB}} = 1.18$ is predicted from molar volumes (as approximated from Equations 4 and 5) for $M = 200$–100,000. This is nearly the observed

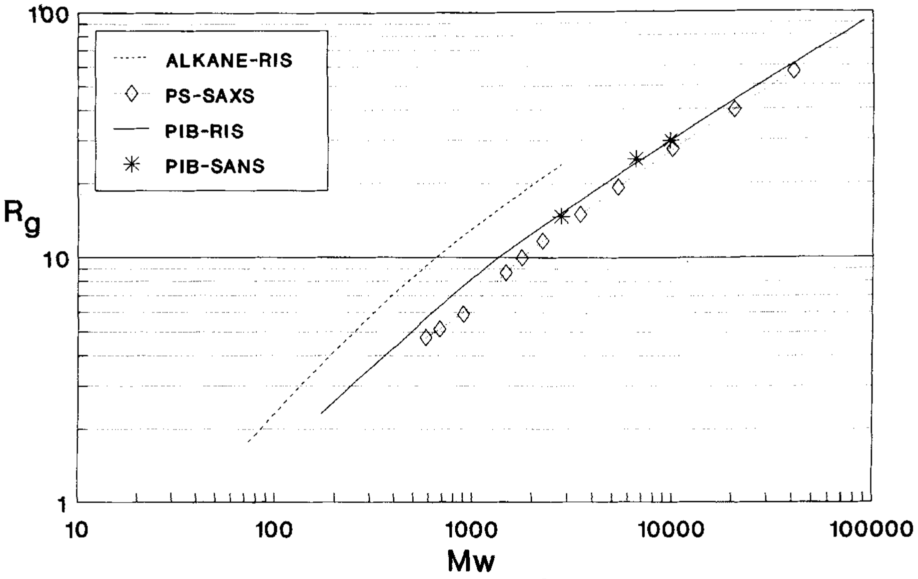

FIGURE 12 Root-mean-square radius of gyration (R_g in Å) vs. M_w for PS, PIB, and alkanes. The PS data (diamonds) are SAXS measurements from reference 8. The PIB data (asterisks) are SANS measurements from the present work. The solid line shows Rotational Isomeric State (RIS) calculations for PIB from the present work (courtesy of L. de Bolt, Exxon). The dashed line shows RIS calculation for n-alkanes are from Tonelli (see text).

result (1.20) even up to molecular weights far above where the van der Waals radii of the molecular contour could be expected to measure the flexible coil size.

Having considered and rejected hydrodynamic and molar volumes, we note that the root-mean-square radius of gyration (R_g) has been, and continues to be, the parameter that naturally arises in the theory of SEC separation [1–3, 43–45]. Unfortunately, very little published R_g data are available in the M range of interest here. In order to supplement this limited data, we have obtained R_g values as calculated from Rotational Isomeric State (RIS) theory. Pearson et al. [46] previously have published *n*-alkane RIS results obtained in a personal communication from Tonelli, which we supplement here with remaining Tonelli results down to pentane. RIS results for PIB down to dimer were obtained in a personal communication from de Bolt, who published results for high M on the same basis [47]. Experimental R_g data for PS are available from Einaga et al. [8]. All of these results are presented in Figure 12. As is clear from the figure (and Table V), our SANS data are in excellent agreement with the de Bolt results for PIB.

Although RIS calculations include atomistic detail to describe intramolecular rotational potentials, bond lengths, and angles, all of the mass of the polymer units is placed on the backbone contour for the purpose of forming the sums. Neglecting the cross-section of the molecule in this way has little effect at high M, but becomes important for low M. Einaga et al. [8] correct for this effect in their PS studies. At DP = 5, the correction is about 1.3 Å or 30% of R_g. In their calculations R_g becomes 0 at DP = 1 (see fig. 9 of reference 8). This concentration of the mass along the backbone is obviously an approximation, which is largest for PS, less for PIB, and small for the *n*-alkanes. For this reason we have chosen to use the experimental data for PS, which actually agrees well with theory at $M \sim 1500$, where the mass placement issue should become unimportant, before diverging again at high M for other reasons. In fact, the PS used by Einaga et al. [8] and the PS which we obtained from PL should be structurally identical, since both are polymerized with *n*-butyl-Li as the anionic initiator. The first 57 units of M is *n*-butyl so that monomer and dimer of our "PS" are about 35 and 21% "*n*-alkane." As M drops in that series, the real R_g has to move toward the *n*-alkane line in Figure 12 and should intercept it at $M = 58$. This may explain the inflexion in the PS R_g data [8] beginning at $M \sim 700$, and could also affect the $[\eta]$ results. However, the *measured* $[\eta]M$ should superimpose regardless of the polymer structure, *if UC is valid.*

In Figures 13 and 14, we use the R_g data from Figure 12 (interpolating as necessary) to construct R_g-based "universal" calibration curves analogous to the V_h curves of Figures 10 and 11. PS results are restricted to $M > 500$ because of the available R_g data (Figure 12). Nevertheless, it is clear than an R_g approach is superior to V_h for the PS/PIB pair. However, the alkane results are well removed from the PS and PIB curves. We conclude that neither V_h nor R_g give a size measure which completely superposes the results for these three polymer types, in spite of the fact that they are all "flexible coils" [29].

The failure for R_g from RIS calculations at very low M may be anticipated as follows. For the High Resolution column set, the PIB trimer at $M = 168$ with 6 backbone carbons elutes at a time only slightly later than the alkane of essentially the same M with 12 backbone carbons. The difference in elution time is consider-

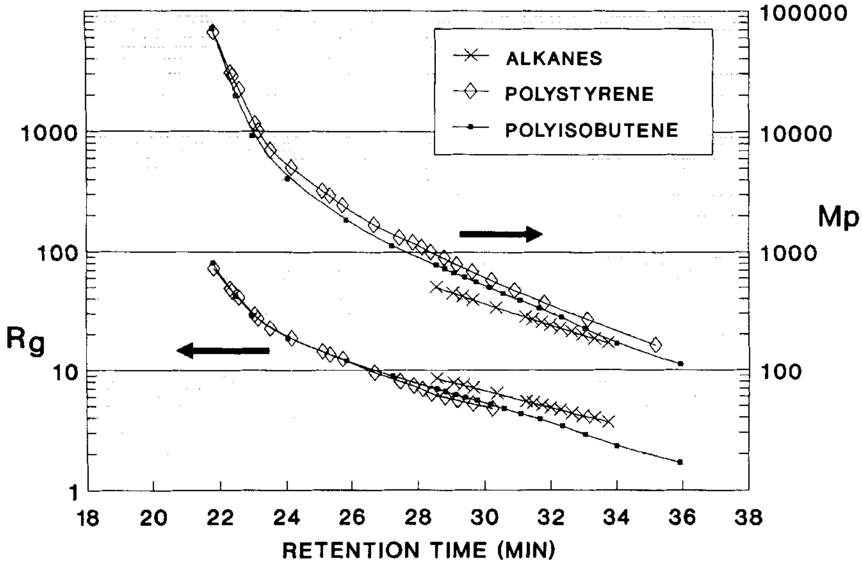

FIGURE 13 SEC calibration curves and R_g-based calibration curves for PS, PIB, and alkanes on High Resolution columns, derived and presented in analogous manner to Figure 10. See text for discussion of derivation of R_g values for individual samples.

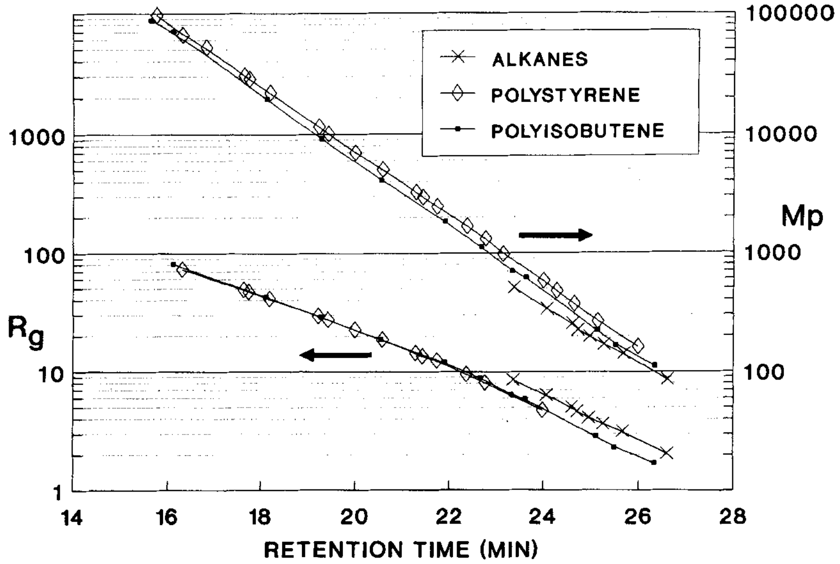

FIGURE 14 SEC calibration curves and R_g-based calibration curves for PS, PIB, and alkanes on Linear columns, derived and presented in analogous manner to Figure 11. See text for discussion of derivation of R_g values for individual samples.

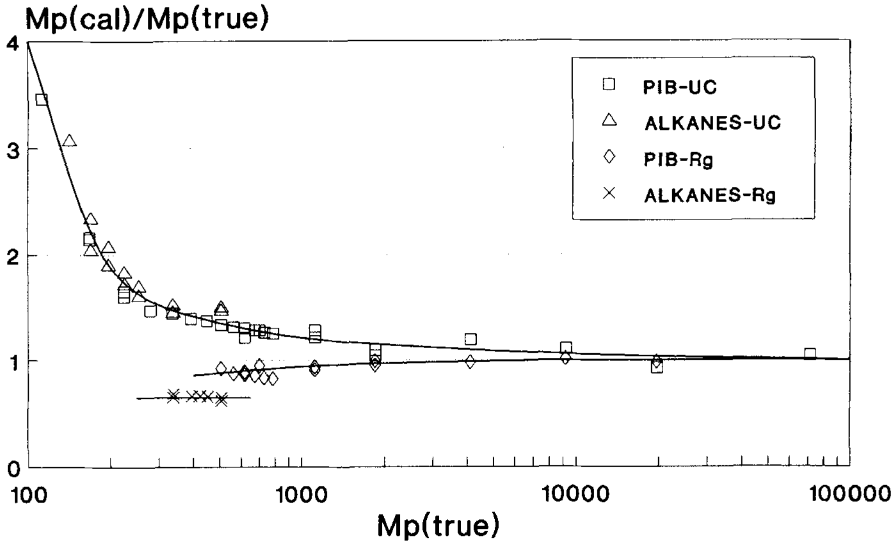

FIGURE 15 Results of calculations of M_p for PIB and alkanes with universal calibration (upper curve, based on V_h) and R_g-based calibration (lower curve), both with PS as the "universal" reference material. For the R_g-based calibration, results are restricted to $M > 500$ because of the available R_g data for PS. The lines through the data are guides for the eye. Results for the two column sets were essentially indistinguishable; both are given in the figure, but for simplicity are not separately labeled.

ably less than that caused by a change of ±1 backbone carbon in either polymer. Obviously, more than an overall R_g calculated with the mass concentrated on the backbone is important in determining the elution time. In terms of realistic RIS potentials, there is no way that a 6-carbon chain can appear as large as a 12-carbon chain as the SEC elution times imply.

In the absence of an accurate normalizing parameter, we can ask how large are the errors incurred if one postulates that V_h or R_g is a proper measure. Those results are given in Figure 15. We have chosen to make PS the reference polymer, because PS standards are far more available than PIB and because *n*-alkanes are soluble in THF at 32°C only over a limited M range. Thus in Figure 15 we plot the ratio of the calculated M_p (from the PS $[\eta]M_p$ or R_g vs. elution time plot) to the true M_p vs. the true M_p for PIB or the *n*-alkanes. To obtain the calculated M_p, we use the measured $[\eta]$ for PIB or the alkanes on the one hand and the R_g vs. M relations for PIB or the *n*-alkanes on the other. Recall the latter is a combination of RIS and experimental data. For example, a PIB sample, whose M is known, is run to get its elution time. That time is used to evaluate an R_g from the PS R_g vs. elution time plot. That R_g is used to evaluate an estimated $M_{\mathrm{PIB}}^{\mathrm{CAL}}$ for the PIB sample with the PIB R_g–M relationship. We then plot $M_{\mathrm{PIB}}^{\mathrm{CAL}}/M_{\mathrm{PIB}}^{\mathrm{TRUE}}$ versus $M_{\mathrm{PIB}}^{\mathrm{TRUE}}$. The R_g approach works better than V_h for PIB versus PS, but apparently begins to fail at low M with a 5–10% underestimate occurring at $M \sim 600$. For the V_h approach, a 10% error (overestimate) is already made at M as high as 5000; at that M the R_g approach looks good for the PS/PIB comparison.

For *n*-alkanes, the R_g approach appears to give nearly as large an underestimate at $\sim M = 600$, as V_h provided an overestimate. As the PIB and *n*-alkane data are not superposed in R_g vs. elution time in Figures 13 and 14 over the whole range they are compared, one must conclude that the R_g approach is actually worse than V_h for superposing PIB and the alkanes. This result is somewhat surprising. There is an indication that the "R_g universal behavior" improves as M increases and the cross-sectional area of the chain becomes less important, but it does not appear that the alkane behavior will merge with PS and PIB until $M > 3000$ (see Figure 13), considerably beyond where the "side group contribution" to R_g is important. Perhaps the fluctuations in conformations about the average R_g are large enough so that a significant population of shapes accessible to the pores exist for the alkanes. For short chains, the fluctuations about R_g average should be large. However, for the molecules with bulky side groups, there should be fewer configurations available that would permit entry into narrow pores.

At high M since $[\eta]\ M \approx \Phi R_g^3$ and the Fox-Flory Φ is constant, [1, 9] the two approaches should give the *same* result, which could be either an incorrect or correct result. It is seen in Figure 15 that, in fact, the ratio of calculated to true M does in fact tend to 1.0 at high M in both cases. We cannot obtain data on higher M alkanes because of their insolubility. At lower M, beginning at $M \sim 5000$ for the V_h prediction and at about 1000 for R_g, the M_p predictions become quite poor. Universal calibration based on V_h does not work and at M_p equals 1000 the error exceeds 25% and reaches 300% at the PIB dimer. With PS as reference the predictions are all too high. Discrepancies arise at low M where Φ is no longer constant and start to increase as M decreases. Einaga et al. [9] have evaluated Φ for PS. Qualitatively, the behavior of Φ for PS is consistent with the deviations observed in Figure 15, if we assume R_g is the correct parameter for SEC separation.

If we construct an SEC calibration curve based on the PS $[\eta]M_p$ values and analyze polydisperse PIB samples, we find for APS6K (see Table IV) an M_n value of 2680, which is 25% too high, and an M_w value of 6380, which is 3% too high. Another example is PPIB1 ($M_n = 1750$, $M_w = 4400$), where overestimations of 25 and 6%, respectively, are found. RI corrections are made in both these cases. If our PS-based UC is used and the RI correction is ignored, the M_n error for both of these PIB samples is over 35%. We could not perform an analogous exercise for R_g because of lack of R_g data for PS below $M = 500$.

Because of the approximations made in the RIS calculations, it is possible that an exact result might reduce the errors further in the R_g measure of elution time. However, it is known that there are specific solvent effects which are not addressed in the RIS calculations so perhaps it is unrealistic to hope for better agreement by including the chain cross-section alone. Experimental R_g data for PIB and the alkanes would provide a better test.

With PS as the reference, the V_h and R_g derived results bracket the correct molecular weights. For V_h, PIB and alkane data show very similar deviations from PS in the V_h analysis (see Figures 10 and 11). Thus if PIB or n-alkanes were chosen as the reference, the molecular weight of the other would be predicted fairly well by UC, but not as well by an R_g approach (see Figures 13 and 14). It will be interesting to see whether other backbones follow the PIB-alkane pattern with PS being unusual in the V_h analysis or will there be a variety of behaviors? *It is clear that PS is a poor choice for a reference material if UC is to be applied to the*

SEC analysis of polyalkenes containing any significant amount of polymer with M less than 1000 *g/mol.*

With the advances being made in molecular dynamics simulations, it should not be long before atomistic modeling of partitioning in pores can aid in predicting how one polymer type behaves compared with another. There may be no single simple measure, [29] but behavior should be predictable, and some features not previously considered may be identified. The fluctuations about the "average" configuration noted above surely can be studied by this technique. It will be interesting to see whether the distinct difference between the alkanes and PIB in Figures 13 and 14 can be explained, and in particular why alkanes have such a large R_g at a given elution time. We are pursuing these issues via molecular dynamics simulations. As this manuscript goes to press, we are finding that MD simulated partitioning of PS and PIB in cylindrical pores, interpreted in terms of an effective radius, provide a much improved explanation of the elution behavior compared to UC or Rg predictions [48].

CONCLUSIONS

In this study we have presented refractive index, specific refractive index increment, and viscosity molecular weight data for PS and PIB, and viscosity-molecular weight data for *n*-alkanes on the same basis. We have quantified the effect of refractive index variation with molecular weight on SEC measurements of M_n and M_w. We have demonstrated the failure of the universal calibration principle in SEC at low molecular weights. We have also examined radii of gyration as a SEC separation parameter and have quantified the magnitude of the errors made if these measures of molecular size are used. The radius of gyration from RIS calculations is superior to the hydrodynamic radius as a predictive parameter, with the two approaches bracketing the correct result. *For SEC determinations of molecular weight averages at low molecular weights, there is no substitute for calibration referenced directly or indirectly to standards of the same chemical structure as the unknowns to be measured, when accuracy needs to be better than* $\pm 20\%$.

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This paper is dedicated to the memory of Dr. Stanley Baniukiewicz, who passed away suddenly in February 1993. Many of the original ideas and observations contained herein were his. Stan's passing is a great loss to all of us, both as a friend and as a scientist.

References

1. C. Booth and C. Price, eds., *Comprehensive Polymer Science, Volume 1, Polymer Characterization* (Pergamon Press, New York, 1989).
2. H. Barth and J. Mays, eds., *Modern Methods of Polymer Characterization* (Wiley, New York, 1991).
3. A. Cooper, ed., *Determination of Molecular Weight* (Wiley, New York, 1989).
4. R. A. Rhein and D. D. Lawson, *Chem Technol.*, **1**, 122, 1971; see also J. P. Menin and R. Roux, *J. Polym. Sci. A-1*, **10**, 855, 1972.
5. F. Candau, J. Francois, and H. Benoit, *Polymer*, **15**, 626, 1974.
6. H. L. Wagner and C. A. J. Hoeve, *J. Polym. Sci. A-2*, **9**, 1763, 1971.
7. E. M. Barrall, M. J. R. Cantow, and J. F. Johnson, *J. Appl. Polym. Sci.*, **12**, 1373, 1968.
8. Y. Einaga, H. Koyama, T. Konishi, and H. Yamakawa, *Macromol.*, **22**, 3419, 1989; F. Abe, Y. Einaga, T. Mashizaki, and H. Yamakawa, *Macromol. 26*, 1884, 1993 and references therein.
9. T. Konishi, T. Yashizaki, T. Saito, Y. Einaga, and H. Yamakawa, *Macromol.*, **23**, 290, 1990.
10. M. B. Ambler and R. D. Matz, *Chromatogr. Sci.*, **8**, 93, 1977; M. Ambler, *J. Polym. Sci., Polym. Let. Ed.*, **14**, 683, 1976.
11. F. Abe, Y. Einaga, and H. Yamakawa, *Macromol.*, **24**, 4423, 1991.
12. R. A. Sanayei and K. F. O'Driscoll, *J. Macromol. Sci. Chem.*, **A28**, 987, 1991.
13. T. Spychaj, D. Lath, and D. Berek, *Polymer*, **20**, 437, 1979.
14. I. Puskas, E. M. Banas, and A. G. Nerheim, *J. Polym. Sci., Symp. Ed.*, **56**, 191, 1976.
15. T. Provder, ed., ACS Symp. Ser. **521**, 1993; T. Provder, ed., ACS Symp. Ser. **352**, 1987.
16. A. E. Hamielec and A. C. Ouano, *J. Liq. Chromatogr.*, **1**, 111, 1978.
17. J. W. Lorimer and D. E. G. Jones, *Polymer*, **13**, 52, 1972.
18. R. Weast, ed., *CRC Handbook of Chemistry and Physics* (CRC Press, Boca Raton, FL, 1989), 69th ed.
19. D. E. Burge, *J. Appl. Polym. Sci.*, **24**, 293, 1979.
20. M. Huglin in *Light Scattering from Polymer Solutions*, M. Huglin, Ed. (Academic Press, New York, 1972) p. 165.
21. J. M. Evans, *Polym. Eng. Sci.*, **13**, 401, 1983.
22. M. C. Piton, R. G. Gilbert, B. E. Chapman, and P. W. Kuchel, *Macromol.*, **26**, 4472, 1993.
23. J. Brandrup and E. Immergut, eds., *Polymer Handbook*, (Wiley, New York, 1989), 3rd ed.
24. W. Schulz and L. Wheeler, personal communication. Schulz finds $S = 119$ and Wheeler finds $S = 121$ for PIB based on samples derived from commercial polybutene. Wheeler finds $S = 83$ for polystyrene (PL standards).
25. R. A. Sanayei, doctoral thesis, University of Waterloo, Ontario, Canada, 1990.
26. D. Margerison, D. R. Bain, and B. Kiely, *Polymer*, **14**, 133, 1973.
27. R. J. W. LeFevre in *Advances in Physical Organic Chemistry*, V. Gold, ed. (Academic Press, New York, 1965), p. 1.
28. Z. Grubisic, P. Rempp, and H. Benoit, *J. Polym. Sci., Polym. Lett. Ed.*, **5**, 753, 1967.
29. P. L. Dubin, J. Kaplan, B. S. Tian, and M. Mehtay, *J. Chromatogr.*, **515**, 37 (1990), and references therein.
30. P. L. Dubin and J. M. Principi, *Macromol.*, **22**, 1891, 1989.
31. J. M. Goldwasser, ACS Symp. Ser. **521**, 242, 1993.
32. Our M_p assignments for PSS PIB standards are in good agreement with current PSS assignments, the largest difference being about 5%. We report and rely on our own values. See 1994 and later PSS literature for their most recent assignments.
33. L. J. Fetters, N. Hadjichristidis, J. Lindner, J. Mays, and W. Wilson, *Macromol.*, **24**, 3127, 1991, and references therein.
34. P. Mrkvickova, S. Lopour, S. Pokovny, and J. Janca, *Ang. Makromol. Chem.*, **90**, 217, 1980.
35. Based on subsequent viscosity–molecular weight comparisons and SEC measurements, PS standards from American Polymer Standards (Mentor, Ohio) or Polymer Standards Service (Mainz) would also have been a reasonable choices.
36. R. A. Sanayei, K. F. O'Driscoll, and A. Rudin, ACS Symp. Ser., **521**, 2, 1993.
37. J. Armonas, *American Polymer Standards Catalog*, Mentor, Ohio (February 8, 1993).
38. J. Garcia de la Torre and J. J. Freire, *Macromol.*, **15**, 155, 1982.
39. S. Mori and A. Yamakawa, *J. Liq. Chromatogr.*, **3**, 329, 1980.
40. C. Tsitsilianis and A. Dondos, *J. Liq. Chromatogr.*, **13**, 3027, 1990.

41. See, for example, F. N. Larsen, *J. Appl. Polym. Sci.*, **8**, 111, 1969.
42. W. Schulz, *J. Chromatogr.*, **55**, 73, 1971.
43. C. Smith et al., *Anal. Chem.*, **65**, 217R, 1993 and references therein.
44. T. Davidson, U. Suter, and W. Deen, *Macromol.*, **20**, 1141, 1987.
45. P. Cyra, T. Bleha, and A. Romanov, *Polymer*, **29**, 1665, 1988.
46. D. Pearson, G. Ver Strate, E. von Meerwall, and F. Schilling, *Macromol.*, **20**, 1133, 1987.
47. L. de Bolt and U. W. Suter, *Macromol.*, **20**, 1424, 1987.
48. R. H. Boyd, R. R. Chance, and G. Ver Strate, manuscript in preparation.