CHARACTERIZATION OF LOW-MOLECULAR-WEIGHT POLYMERS: FAILURE OF UNIVERSAL CALIBRATION IN SIZE EXCLUSION CHROMATOGRAPHY

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Abstract

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 due to 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, Rg. 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 \(M_w\)'s 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.

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 absolute 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 and light scattering.¹,⁷ The intrinsic viscosity dependence on molecular weight also becomes quite complicated at low-molecular-weights. In fact, polystyrene exhibits amongst 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 relationships¹² 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 CaH₂, then distilled after refluxing over metallic sodium for at least 48 hours. The first 150-200 mL of the distillate, representing about 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 used for chromatography and online viscosity measurements without further treatment. The H₂O 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 H₂O absorption in THF influenced viscosity measurements. The literature suggests that at least several tenths of a percent H₂O would need to be present to cause a significant change in intrinsic viscosity, especially at low-molecular-weight. 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 subjected to the same purification procedure, as was the benzene (Baker, reagent grade) used in a limited number of viscosity measurements for Mₘₜ crosschecks.

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, e.g., 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 ($M_n = 1750$, $M_w/M_n = 2.5$; vide infra) for the lower portion of this molecular weight range is designated PPIB1. One other polydisperse sample (PP1B2) of commercial origin ($M_n = 1260$, $M_w/M_n = 2.0$; vide infra) 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, infra-red 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 \(\eta/\eta_s\) were determined at 25°C and 30°C in THF by using a Schott-Gerate automatic viscometer. The solvent flow time is \(\sim\)110 s for the majority of the measurements reported here and \(\sim\)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 \((\eta - \eta_s)/\eta_{sc}\) to zero concentration, via the Huggins relation:

\[
(\eta - \eta_s)/\eta_{sc} = [\eta] + K_h[\eta]^2c
\]
The \([\eta]\) values obtained on three samples (PL2450, PL10K, and NBS706) were used to calibrate the Viscotek Differential Viscometer Model 110 (though crosschecks 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 \(\Delta P\) 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. No antioxidant was employed. No changes in results were observed for solutions stored at 20°C for periods of several days. The solutions were exposed to fluorescent
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.\textsuperscript{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\textsuperscript{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, i.e., 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., [η] c<1) and to have the total scattering R' at 2-6 times the Rayleigh ratio of heptane, R = 5.64 \cdot 10^{-6} \text{ cm}^{-1}.

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

\[
(Kc/ΔR)^{1/2} = M_w^{-1/2} (1+A_2cM_w)
\]

where K is a known function of n, wavelength, and dn/dc. \(M_w\) was calculated from the intercept of \((Kc/ΔR)^{1/2}\) 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 10.5 Å, 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. 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 ~ 35,000) increased with an approximate 1/√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 ± 40) and sucrose octaacetate (M=678, K = 2155 ± 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 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 ±5%, compared to ±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. For VPO the operating relationship is

\[ \Delta R/c = K(1/M_n + A_2c + A_3c^2 + \ldots) \]

where \( \Delta R \) 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. 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 these high concentrations, there is essentially no A\textsubscript{2} contribution in the case of PIB in toluene over the M\textsubscript{n} range studied here by VPO. Polystyrene under the same conditions exhibits a positive A\textsubscript{2} (\(-10^{-4}\) mL mole/g\textsuperscript{2} at 2500 molecular weight). With systematic behavior in A\textsubscript{2} being observed and a proper thermistor rinsing protocol, which ensures that the instrument zero is well-determined, very 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:\textsuperscript{20}

\[
\text{dn/dc} = \frac{(n_p - n_s)}{d_p}
\]

where n\textsubscript{p} is the polymer refractive index, n\textsubscript{s} is the solvent refractive index and d\textsubscript{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\textsubscript{p}. In good solvents, a somewhat more complicated formula is required.\textsuperscript{5,20} It is well-known that dn/dc varies with the number-average molecular weight of the polymer,\textsuperscript{5,6} and it is easily demonstrated that this variation is due to end-group effects. dn/dc, n\textsubscript{p}, and d\textsubscript{p} vary nearly linearly with 1/M\textsubscript{n}, all approaching asymptotic limits at high-molecular-weight.

Though the effect of the variation of dn/dc with molecular weight on the SEC concentration detector\textsuperscript{7,21} and LS intensity\textsuperscript{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, 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 PP$IB_2$ and PIB$F_2$ 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 the $n_p$ measurements of Rhein and Lawson4 for PIB oligomers $\left(\text{DP} = 2-7\right)$. The linear regressions of the data (excluding PIB trimer and dimer) give the following equations:

\begin{align*}
\text{PIB} & \quad n_p = (1.5092\pm-0.0002) - (13.9\pm-0.1)/M_n \quad (2) \\
\text{PS} & \quad n_p = (1.601\pm-0.002) - (18.8\pm-0.5)/M_n \quad (3)
\end{align*}

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 so derived will be within the stated uncertainties in Equation (2), which correspond to about +/- 100 units at 2000 $M_n$ and about +/- 5000 at 20,000 $M_n$. 

$dn/dc$ 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 Section IV. The calculated dn/dc values are obtained from Equation (1) with the following density functions:

\[
\begin{align*}
\text{PIB} & \quad \d_p = 0.917 (1-30/M_n) \\
\text{PS} & \quad \d_p = 1.08(1 - 33/M_n)
\end{align*}
\]

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 straight line fits correspond to the equations:

\[
\begin{align*}
\text{PIB} & \quad \d_{n/c} = 0.115(1 - 122/M_n) \\
\text{PS} & \quad \d_{n/c} = 0.190(1 - 83/M_n)
\end{align*}
\]

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 ±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 \(S \equiv 90-100\), 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 \(d_p\) (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

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2000 $M_n$) must be explicitly taken into account.\textsuperscript{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).\textsuperscript{14} The specific refractions $[(n^2-1)/(n^2+2)d]$ of, for example, dimers of isobutene 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.\textsuperscript{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;\textsuperscript{20} $n$ and $d$ data for model dimers support this conclusion.\textsuperscript{18} Therefore, the $M_n$ dependence of $dn/dc$, $S$ in Equation (6), is expected to be 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 on SEC and LS

SEC data are corrected for the $dn/dc$ variation by dividing the observed area by $(1 - S/M)$, where $M$ is the molecular weight of the SEC slice.\textsuperscript{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 $1000 \text{ M}_n$, failure to perform the RI correction results in overestimations of $M_n$ by 20\%, 8\%, and 9\% respectively for PIB, PS, and PMMA. At $2000 \text{ M}_n$, 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 results for PS $M_n$ are about twice as large as the RI corrections found by Sanayei and O'Driscol\textsuperscript{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.\textsuperscript{24} Support for our PS results can be found in the work of Barrall et al.\textsuperscript{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 versus 1.4050 at 25°C, but still below $n_p$ of PS for DP$>1$). The $dn/dc$ measurements of Barrall et al. yield $S \approx 170$ for PS in toluene (see also reference 5), which is in close agreement with the value calculated from Equations (1), (3), and (5) (also $S \approx 170$). Barrall et al. find a 13\% overestimation of $M_n$ in SEC analysis of a PS sample in toluene with $M_n = 5400$ and $M_w/M_n \approx 2$. 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 $M_w/M_n \approx 3$, 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 formula:

$$M_w^{\text{obs}} = M_n + (M_w - M_n)/(1-S/M_n)^2$$

This formula assumes that the $dn/dc$ measured for the polydisperse sample is used in the $M_w$ calculation. 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 versus 25°C for $n_p$ and 27°C for $dn/dc$) will 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: $\frac{dn_p}{dT} = 3.0 \times 10^{-4} (1-73/M_n)^{0.9}°\text{C}^{-1}$. Our result for the temperature dependence of the PIB density is $5.5 \times 10^{-4}$ g/mL °C, essentially independent of $M_n$ over the $M_n$ range measured (300-2500). $\frac{dn_s}{dT}$ for THF is $4.4 \times 10^{-4}°\text{C}^{-1}$ with $n_s = 1.405$ at 25°C. If these values are substituted into Equation (1), we find $d(dn/dc)/dT = 2 \times 10^{-4}$ mL/g-°C for PIB at high $M_n$ and about $4 \times 10^{-4}$ for the low DP range. The temperature dependence of $S (dS/dT = -0.45$ g/mol-°
C) is completely negligible for our purposes. We have not evaluated \( d(n/dc)/dt \) 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 SEC1-3,15,16,28 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 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 other29 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.

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 Janca et al.\(^{34}\)

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 merges into that of Janca et al.\(^{34}\) 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 $[\eta] = K M^{1/2} + K'M$, 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.

It is not our intent here to explain this complex behavior of PS. Einaga et al. 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. At very low molecular weight, $[\eta]$ departs towards negative values due to packing effects. Abe et al. simply correct 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 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 (>50,000), we
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 $M_p^\text{PS}$ and $M_p$ for n-alkanes is in quantitative agreement with published data of Mori and Yamakawa.\textsuperscript{39}

Shown in the lower portions of Figures 10 and 11 are UC curves, $V_h = [\eta] M_p$ 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 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,\textsuperscript{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 ref. 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 ±2% for $M_n$ determinations in this SEC calibration process.

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.\textsuperscript{12,40} In our results, there is some hint of departure from UC below 1000, which could not be confirmed because of our lack of authentic oligomers of PMMA.
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Molar volumes\textsuperscript{10,41,42} and "mean projection lengths"\textsuperscript{1,29} have also been used as measures of SEC separation at low-molecular-weights. Although it has been shown\textsuperscript{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 $\pm$ 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 $M_{PS}/M_{PIB} = 1.18$ is predicted from molar volumes (as approximated from Equations 4 and 5) for $M = 200$-100,000. This is nearly the observed 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\textsuperscript{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.\textsuperscript{46} previously have published $n$-alkane RIS results obtained in a personal communication from Tonelli (North Carolina State), 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 (Exxon), who published results for high $M$ on the same basis.\textsuperscript{47} Experimental $R_g$ data for PS are available from Einaga et al.\textsuperscript{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
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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 $[\eta] M = \Phi R_g^3$ and the Fox-Flory $\Phi$ is constant, 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. Interestingly 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 $\Phi$ is no longer constant and start to increase as $M$ decreases. Einaga et al. have evaluated $\Phi$ for PS. Qualitatively, the behavior of $\Phi$ 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 calculation: 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 to another. There may be no single simple measure,\(^{29}\) but behavior should be predictable, and some features not previously considered may be deduced. 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.

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
+20%.

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cooperation, and his comments on this manuscript.

This manuscript 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.
Table I
Refractive Indices for Polyisobutene and Polystyrene
(25.0°C, 589 nm)

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</tbody>
</table>

$^a$ $M_n$ 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 2 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 rough estimate from expected LS and SEC precision.
Table II
Refractive Indices and Refractive Index Increments for Polyisobutene

$M_n$ 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.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$M_n$</th>
<th>$n_p$</th>
<th>dn/dc (THF)$^a$</th>
<th>dn/dc (heptane)$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dimer</td>
<td>112</td>
<td>1.4060</td>
<td>[0.0014]</td>
<td>[0.031]</td>
</tr>
<tr>
<td>Trimer</td>
<td>168</td>
<td>1.4280</td>
<td>[0.0304]</td>
<td>[0.056]</td>
</tr>
<tr>
<td>Tetramer</td>
<td>224</td>
<td>1.4471</td>
<td>[0.0530]</td>
<td>[0.078]</td>
</tr>
<tr>
<td>Pentamer</td>
<td>280</td>
<td>1.4569$^b$</td>
<td>[0.0638]</td>
<td>[0.087]</td>
</tr>
<tr>
<td>Hexamer</td>
<td>336</td>
<td>1.4665$^b$</td>
<td>[0.0739]</td>
<td>[0.097]</td>
</tr>
<tr>
<td>Heptamer</td>
<td>392</td>
<td>1.4721$^b$</td>
<td>[0.0792]</td>
<td>[0.103]</td>
</tr>
<tr>
<td>PIB1</td>
<td>470</td>
<td>1.4805</td>
<td>0.0868 [0.0878]</td>
<td>-</td>
</tr>
<tr>
<td>PIB2</td>
<td>690</td>
<td>1.4901</td>
<td>0.0961 [0.0968]</td>
<td>-</td>
</tr>
<tr>
<td>PIB3</td>
<td>810</td>
<td>1.4925</td>
<td>0.0992 [0.0990]</td>
<td>-</td>
</tr>
<tr>
<td>PIB4</td>
<td>960</td>
<td>1.4949</td>
<td>0.1013 [0.1011]</td>
<td>-</td>
</tr>
<tr>
<td>PIB5</td>
<td>1110</td>
<td>1.4966</td>
<td>0.1029 [0.1027]</td>
<td>0.133 [0.125]</td>
</tr>
<tr>
<td>PIB6</td>
<td>1300</td>
<td>1.4987</td>
<td>0.1050 [0.1045]</td>
<td>-</td>
</tr>
<tr>
<td>PIB7</td>
<td>1540</td>
<td>1.5003</td>
<td>0.1061 [0.1059]</td>
<td>-</td>
</tr>
<tr>
<td>PIB8</td>
<td>1800</td>
<td>1.5015</td>
<td>0.1075 [0.1070]</td>
<td>-</td>
</tr>
<tr>
<td>PIB9</td>
<td>2130</td>
<td>1.5026</td>
<td>0.1086 [0.1080]</td>
<td>-</td>
</tr>
<tr>
<td>PIB10</td>
<td>3300</td>
<td>1.5047</td>
<td>0.1125 [0.1098]</td>
<td>0.137 [0.131]</td>
</tr>
<tr>
<td>PIB11</td>
<td>5000</td>
<td>1.5058</td>
<td>0.1086 [0.1107]</td>
<td>0.138 [0.132]</td>
</tr>
<tr>
<td>PIB14</td>
<td>13000</td>
<td>1.5078</td>
<td>0.1122 [0.1123]</td>
<td>0.142 [0.134]</td>
</tr>
<tr>
<td>PIB15</td>
<td>35000</td>
<td>1.5087</td>
<td>0.1131 [0.1132]</td>
<td>0.143 [0.135]</td>
</tr>
</tbody>
</table>

$^a$ Calculated values based on $n_p$ and $d_p$ (see Equation 1) are shown in brackets (25°C, 589 nm). Units are mL/g.

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

Refractive Indices and Refractive Index Increments for Polystyrene

np measurements at 589 nm; dn/dc measurements at 633 nm in THF.

All measurements at 25°C.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$M_n$</th>
<th>$n_p$</th>
<th>$dn/dc$ (cal)$^a$</th>
<th>$dn/dc$ (meas)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PL162</td>
<td>162</td>
<td>1.4849</td>
<td>0.093</td>
<td>-</td>
</tr>
<tr>
<td>PS266</td>
<td>266</td>
<td>1.5302</td>
<td>0.132</td>
<td>-</td>
</tr>
<tr>
<td>PS370</td>
<td>370</td>
<td>1.5505</td>
<td>0.148</td>
<td>-</td>
</tr>
<tr>
<td>PL580</td>
<td>550</td>
<td>1.5664</td>
<td>0.159</td>
<td>0.154</td>
</tr>
<tr>
<td>PL1700</td>
<td>1590</td>
<td>-</td>
<td>-</td>
<td>0.187</td>
</tr>
<tr>
<td>PL2450</td>
<td>2320</td>
<td>-</td>
<td>-</td>
<td>0.187</td>
</tr>
</tbody>
</table>

$^a$ Calculated $dn/dc$ based on $n_p$ and $d_p$ (see Equation 1). Units are mL/g.
Table IV
Effect of Refractive Index Correction on $M_n$ and $M_w$ Determinations for Polydisperse PIB APS6K in THF

<table>
<thead>
<tr>
<th>Supplier M</th>
<th>Corrected</th>
<th>Uncorrected</th>
<th>Overestimation(^a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$M_n$-SEC</td>
<td>2060</td>
<td>2140</td>
<td>2470</td>
</tr>
<tr>
<td>$M_w$-SEC</td>
<td>5900</td>
<td>6190</td>
<td>6420</td>
</tr>
<tr>
<td>$M_w$-LS(^b)</td>
<td>5900</td>
<td>6190</td>
<td>6690</td>
</tr>
</tbody>
</table>

\(^a\)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).
Table V
Polyisobutene
Molecular Weights, Intrinsic Viscosities, Polydispersities and Radii of Gyration
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>
<thead>
<tr>
<th>Sample</th>
<th>$M_n$</th>
<th>$M_w$</th>
<th>$[\eta]$ dL/g</th>
<th>$M_p$ (Assigned)</th>
<th>$M_w/M_n$ (SEC)</th>
<th>$M_w$</th>
<th>$R_g$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dimer</td>
<td>112a</td>
<td></td>
<td>0.0036</td>
<td>112</td>
<td>1.00</td>
<td>112</td>
<td>1.6</td>
</tr>
<tr>
<td>Trimer</td>
<td>168a</td>
<td></td>
<td>0.009</td>
<td>168</td>
<td>1.01</td>
<td>168</td>
<td>2.3</td>
</tr>
<tr>
<td>Tetramer</td>
<td>224a</td>
<td></td>
<td>0.014</td>
<td>224</td>
<td>1.01</td>
<td>224</td>
<td>2.8</td>
</tr>
<tr>
<td>PIB1</td>
<td>473b</td>
<td></td>
<td>0.024</td>
<td></td>
<td>1.19</td>
<td>560</td>
<td></td>
</tr>
<tr>
<td>PIB2</td>
<td>730b</td>
<td></td>
<td>0.030</td>
<td>700c</td>
<td>1.16</td>
<td>790</td>
<td>6.3</td>
</tr>
<tr>
<td>PIB3</td>
<td>830b</td>
<td></td>
<td>0.032</td>
<td></td>
<td>1.18</td>
<td>940</td>
<td></td>
</tr>
<tr>
<td>PIB4</td>
<td>970b</td>
<td></td>
<td>0.035</td>
<td></td>
<td>1.21</td>
<td>1160</td>
<td></td>
</tr>
<tr>
<td>PIB5</td>
<td>1100b</td>
<td>1400d</td>
<td>0.039</td>
<td></td>
<td>1.18</td>
<td>1310</td>
<td></td>
</tr>
<tr>
<td>PIB6</td>
<td>1320b</td>
<td></td>
<td>0.041</td>
<td></td>
<td>1.20</td>
<td>1520</td>
<td></td>
</tr>
<tr>
<td>PIB7</td>
<td>1560b</td>
<td></td>
<td>0.045</td>
<td></td>
<td>1.17</td>
<td>1780</td>
<td></td>
</tr>
<tr>
<td>PIB8</td>
<td>1810b</td>
<td></td>
<td>0.048</td>
<td></td>
<td>1.15</td>
<td>2050</td>
<td></td>
</tr>
<tr>
<td>PIB9</td>
<td>2110b</td>
<td></td>
<td></td>
<td></td>
<td>1.15</td>
<td>2520</td>
<td></td>
</tr>
<tr>
<td>PIB10</td>
<td>3100b</td>
<td>4300d</td>
<td>0.070</td>
<td></td>
<td>1.30</td>
<td>4300</td>
<td></td>
</tr>
<tr>
<td>PIB11</td>
<td></td>
<td>7200d</td>
<td>0.087</td>
<td></td>
<td>1.23</td>
<td>6600</td>
<td></td>
</tr>
<tr>
<td>PIB12</td>
<td></td>
<td>6400e</td>
<td></td>
<td></td>
<td>1.21</td>
<td>6600</td>
<td>24.4</td>
</tr>
<tr>
<td>PIB13</td>
<td></td>
<td>9700e</td>
<td></td>
<td></td>
<td>1.20</td>
<td>9800</td>
<td>29.7</td>
</tr>
<tr>
<td>PIB14</td>
<td></td>
<td>58000d</td>
<td>0.30</td>
<td></td>
<td>4.10</td>
<td>60000</td>
<td></td>
</tr>
<tr>
<td>PIB15</td>
<td>28000b</td>
<td>65000d</td>
<td>0.36</td>
<td>2.00</td>
<td>70000</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PIBF1</td>
<td>2300b</td>
<td>3000d</td>
<td></td>
<td>1.23</td>
<td>2900</td>
<td>15.2</td>
<td></td>
</tr>
<tr>
<td>PSS616</td>
<td>550b,570f</td>
<td></td>
<td>0.026</td>
<td>616c</td>
<td>1.10</td>
<td>650</td>
<td>5.5</td>
</tr>
<tr>
<td>PSS1K</td>
<td>1050b,1030f</td>
<td></td>
<td>0.037</td>
<td>1120</td>
<td>1.06</td>
<td>1170</td>
<td>8.5</td>
</tr>
<tr>
<td>PSS2K</td>
<td>1830b,2000f</td>
<td></td>
<td>0.052</td>
<td>1850</td>
<td>1.16</td>
<td>2300</td>
<td>12.0</td>
</tr>
<tr>
<td>PSS4K</td>
<td>2630b,2800f</td>
<td></td>
<td>0.070</td>
<td>4100</td>
<td>1.40</td>
<td>4300</td>
<td>18.6</td>
</tr>
<tr>
<td>PSS10K</td>
<td></td>
<td>8700d</td>
<td>0.110</td>
<td>9200</td>
<td>1.21</td>
<td>9600</td>
<td>29.6</td>
</tr>
<tr>
<td>PSS20K</td>
<td></td>
<td>18000d</td>
<td>0.189</td>
<td>19600</td>
<td>1.16</td>
<td>23000</td>
<td>42.5</td>
</tr>
<tr>
<td>PSS71K</td>
<td></td>
<td></td>
<td>0.39</td>
<td>71000</td>
<td>1.17</td>
<td>66000</td>
<td>81.0</td>
</tr>
<tr>
<td>PSS86K</td>
<td></td>
<td></td>
<td>0.47</td>
<td>87,600g</td>
<td>1.15</td>
<td>860000g</td>
<td></td>
</tr>
<tr>
<td>PSS108K</td>
<td></td>
<td></td>
<td>0.58</td>
<td>108,000g</td>
<td>1.13</td>
<td>1120000g</td>
<td></td>
</tr>
<tr>
<td>APS160K</td>
<td></td>
<td></td>
<td>0.61</td>
<td></td>
<td>1.21</td>
<td>1600000g</td>
<td></td>
</tr>
<tr>
<td>APS247K</td>
<td></td>
<td></td>
<td>0.87</td>
<td></td>
<td>1.20</td>
<td>2470000g</td>
<td></td>
</tr>
<tr>
<td>APS300</td>
<td>310b</td>
<td></td>
<td>0.019</td>
<td></td>
<td>1.16</td>
<td>360</td>
<td></td>
</tr>
<tr>
<td>APS6K</td>
<td>2080b</td>
<td></td>
<td>0.082i</td>
<td></td>
<td>2.90</td>
<td>6190</td>
<td></td>
</tr>
<tr>
<td>PP1B1</td>
<td>1780b</td>
<td></td>
<td>0.068</td>
<td></td>
<td>2.50</td>
<td>4300</td>
<td></td>
</tr>
<tr>
<td>PP1B2</td>
<td>1275b,1260j</td>
<td></td>
<td>0.054</td>
<td></td>
<td>2.00</td>
<td>2600</td>
<td></td>
</tr>
</tbody>
</table>

a Confirmed by GC mass spectroscopy.
b $M_n$ determined based on 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 D1 (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 obtains 3300 by VPO for PSS4K.
g $M_w$ and $M_p$ values for these four standards are from the suppliers (Polymers Standards Service and American Polymer Standards). They are fairly consistent with our THF and benzene $[\eta]$ data and published $[\eta]$-M relationships for these solvents (ref. 11, 33, and 34), which suggest $M_w$ values of 95K, 120K, 145K, and 220K.
h Interpolated, based on $M_p$, from de Bolt RIS results (ref. 47) which were available for integer degrees of polymerization. Values in brackets for three samples are SANS measurements in deuterated decane.
i This sample gave identical results in the Viscotech and a suspended-level viscometers.
j VPO - See Table I.
### Table VI

**Polystyrene**

Molecular Weights, Polydispersities, Intrinsic Viscosities, and Radii of Gyration

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

<table>
<thead>
<tr>
<th>Sample</th>
<th>M_W</th>
<th>M_W/M_n</th>
<th>M_p</th>
<th><a href="dL/g">η</a>^c</th>
<th>R_g(Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PL162</td>
<td>162</td>
<td>1.0</td>
<td>162</td>
<td>0.0117</td>
<td>-</td>
</tr>
<tr>
<td>PS266^a</td>
<td>266</td>
<td>1.0</td>
<td>266</td>
<td>0.0181</td>
<td>-</td>
</tr>
<tr>
<td>PS370^a</td>
<td>370</td>
<td>1.0</td>
<td>370</td>
<td>0.0219</td>
<td>-</td>
</tr>
<tr>
<td>PS474^a</td>
<td>474</td>
<td>1.0</td>
<td>474</td>
<td>0.0238</td>
<td>-</td>
</tr>
<tr>
<td>PL580</td>
<td>650</td>
<td>1.16</td>
<td>580</td>
<td>0.0265</td>
<td>4.75</td>
</tr>
<tr>
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<td>1020</td>
<td>1.09</td>
<td>980</td>
<td>0.0305</td>
<td>-</td>
</tr>
<tr>
<td>PL1320</td>
<td>1300</td>
<td>1.07</td>
<td>1320</td>
<td>0.0341</td>
<td>8.05</td>
</tr>
<tr>
<td>PL1700^b</td>
<td>1670</td>
<td>1.06</td>
<td>1700</td>
<td>0.0388</td>
<td>9.55</td>
</tr>
<tr>
<td>PL2450^b</td>
<td>2410</td>
<td>1.05</td>
<td>2450</td>
<td>0.0457 (0.044)</td>
<td>12.4</td>
</tr>
<tr>
<td>PL2950^b</td>
<td>2970</td>
<td>1.05</td>
<td>2950</td>
<td>0.0497</td>
<td>13.5</td>
</tr>
<tr>
<td>PL3250</td>
<td>3210</td>
<td>1.04</td>
<td>3250</td>
<td>0.0527</td>
<td>14.4</td>
</tr>
<tr>
<td>PL5K</td>
<td>5000</td>
<td>1.05</td>
<td>5050</td>
<td>0.0647</td>
<td>18.6</td>
</tr>
<tr>
<td>PL7K</td>
<td>7100</td>
<td>1.04</td>
<td>7000</td>
<td>0.0772</td>
<td>22.5</td>
</tr>
<tr>
<td>PL10K</td>
<td>9900</td>
<td>1.03</td>
<td>10,100</td>
<td>0.0937 (0.093)</td>
<td>27.4</td>
</tr>
<tr>
<td>PL12K</td>
<td>11,700</td>
<td>1.03</td>
<td>11,600</td>
<td>0.1033</td>
<td>29.6</td>
</tr>
<tr>
<td>PL22K</td>
<td>22,100</td>
<td>1.03</td>
<td>22,000</td>
<td>0.155</td>
<td>41.0</td>
</tr>
<tr>
<td>PL29K</td>
<td>28,600</td>
<td>1.03</td>
<td>28,500</td>
<td>0.180</td>
<td>47.0</td>
</tr>
<tr>
<td>PL30K</td>
<td>30,200</td>
<td>1.03</td>
<td>30,300</td>
<td>0.193</td>
<td>49.0</td>
</tr>
<tr>
<td>PL52K</td>
<td>51,000</td>
<td>1.03</td>
<td>52,000</td>
<td>0.275</td>
<td>-</td>
</tr>
<tr>
<td>PL66K</td>
<td>66,000</td>
<td>1.03</td>
<td>66,000</td>
<td>0.332</td>
<td>73.0</td>
</tr>
<tr>
<td>PL96K</td>
<td>94,000</td>
<td>1.04</td>
<td>96,000</td>
<td>0.433</td>
<td>-</td>
</tr>
<tr>
<td>NBS706</td>
<td>276,000</td>
<td>-</td>
<td>-</td>
<td>0.88 (0.88)^e</td>
<td>-</td>
</tr>
</tbody>
</table>

- 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).
- 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).
- THF at 30°C. This study, Viscotek, except for values shown in parentheses for three samples, which were obtained on suspended-level viscometer.
- Values interpolated, based on M_p, from experimental results of Einaga et al.\(^8\), no experimental R_g data available below M=580.
- Literature values for [η] 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.
Table VII

n-Alkanes
Molecular Weights, Intrinsic Viscosities, and Radii of Gyration

<table>
<thead>
<tr>
<th># of Carbons</th>
<th>M^a</th>
<th>\ln(cL/g)^b</th>
<th>R_g(Å)^c</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>142</td>
<td>0.0063</td>
<td>3.15</td>
</tr>
<tr>
<td>12</td>
<td>170</td>
<td>0.0106</td>
<td>3.62</td>
</tr>
<tr>
<td>14</td>
<td>198</td>
<td>0.0137</td>
<td>4.10</td>
</tr>
<tr>
<td>16</td>
<td>226</td>
<td>0.0173</td>
<td>4.10</td>
</tr>
<tr>
<td>18</td>
<td>254</td>
<td>0.0195</td>
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<tr>
<td>24</td>
<td>338</td>
<td>0.0275</td>
<td>6.34</td>
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<tr>
<td>36</td>
<td>506</td>
<td>0.0381</td>
<td>8.50</td>
</tr>
</tbody>
</table>

a  These samples are monodisperse.
b  THF at 30°C, this study.
c  Personal communication from Tonelli; data at 30°C.
References


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32. Our $M_p$ assignments for PSS PIB standards are in good agreement with PSS, the largest difference being about $\%$. We report and rely on our own values. See 1994 PSS literature for their most recent assignments.


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.


37. J. Armonas, American Polymer Standards Catalog, Mentor, Ohio (February 8, 1993).


