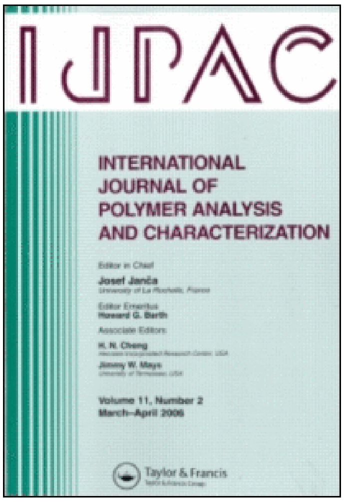

International Journal of Polymer Analysis and Characterization
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713646643

Solution Characterization of Monodisperse Atactic Polystyrenes by Static and Dynamic Light Scattering

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To cite this Article Min, G. , Savin, D. , Gu, Z. , Patterson, G. D. , Kim, S. H. , Ramsay, D. J. , Fishman, D. , Ivanov, I. , Sheina, E. , Slaby, E. and Oliver, J.(2003) 'Solution Characterization of Monodisperse Atactic Polystyrenes by Static and Dynamic Light Scattering', International Journal of Polymer Analysis and Characterization, 8: 3, 187 — 207

To link to this Article: DOI: 10.1080/10236660304875

URL: http://dx.doi.org/10.1080/10236660304875

International Journal of Polymer Anal. Charact., 8: 187–207, 2003

1023-666X/03 $12.00 + .00
DOI: 10.1080/10236660390128346

Solution Characterization of Monodisperse Atactic Polystyrenes by Static and Dynamic Light Scattering

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Anionically polymerized polystyrene standards have been characterized by static and dynamic light scattering in toluene at 25°C. The molecular weights ranged from 3000 to two million g/mol. An appropriate standard for light scattering intensity was developed and the absolute Rayleigh ratio for toluene was determined for the experimental conditions. The molecular weight dependence of the second virial coefficient A_2 *could be represented as a power law. The present results are in good agreement with previous measurements of* A_2*. For the higher molecular weight polymers, the mean-square radius of gyration was determined. The present results could also be represented as a power law, which was in good agreement with previous results. Dynamic light scattering was analyzed to obtain the mutual-diffusion coefficient as a function of concentration and molecular weight. These results were then used to obtain the self-diffusion coefficient, hydrodynamic radius, and virial coefficient for the mutual-diffusion coefficient. Hydrodynamic radii could be represented as a power law, which was also in good agreement with previous reports. The virial coefficient for the mutual friction was calculated as well. The relationship between*

Received 30 August 2001; accepted 10 December 2001.

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The study of the systematic properties of a homologous series of chain molecules requires a consistent set of polymers. The authors would like to thank Pressure Chemical Company, which has for many years synthesized anionic polystyrenes of very narrow molecular weight distribution. The present project was carried out with their support and encouragement.

molecular weight distribution and the polydispersity index determined from dynamic light scattering was calculated and compared to actual data. The samples used here conformed to the manufacturers' reported weight to number-average molecular weight ratios.

Keywords: Polystyrene characterization; Light scattering; Radius of gyration; Hydrodynamic radius; Osmotic second virial coefficient; Self-diffusion coefficient; Molecular weight distributions; Molecular weight scaling laws

INTRODUCTION

Light scattering has long been employed as a standard technique for measuring the weight-average molecular weight M_w of polymers in solution[1]. If the mean-square radius of gyration $\langle R_G^2 \rangle$ of the chains is sufficiently large, static light scattering can be used to obtain the z-average of this quantity. The osmotic second virial coefficient A_2 is also obtained from light-scattering data and is a function of molecular weight. Dynamic light scattering[2] can be used to obtain the z-average hydrodynamic radius $\langle R_h \rangle_z$. The explicit molecular weight dependence of these three quantities has been discussed at length in a review[3]. The existence of a large set of narrow molecular weight distribution polystyrenes has made possible another systematic study of this problem. The present article addresses details necessary to carry out a thorough systematic study of the molecular weight dependence of polymer properties in solution.

Although light scattering is usually considered an absolute method of molecular weight determination, in actual practice all measurements are carried out relative to some standard. The polymer is dissolved in a solvent of known scattering cross section, $R^0(T, \lambda)$. The excess scattering by the solution is determined and converted to an absolute Rayleigh ratio, $\Delta R(q, c)$:

$$\Delta R(q, c) = \frac{I(q, c) - I^0}{I^0} R^0(T, \lambda) \tag{1}$$

The magnitude of the scattering vector is given by

$$q = \left(\frac{4\pi n}{\lambda}\right) \sin\frac{\theta}{2} \tag{2}$$

where n is the refractive index of the solution, λ is the wavelength of the incident light in a vacuum, and θ is the scattering angle. The dependence of refractive index on concentration dn/dc can be measured. The excess Rayleigh ratio can be represented as

$$\Delta R(q,c) = KcMS(q,c) \tag{3}$$

where $K = \left(\frac{4\pi^2}{\lambda^4 N_A}\right) n^2 \left(\frac{dn}{dc}\right)^2$, and S(q, c) is the scattering function per molecule. In the Zimm limit $(q \to 0, c \to 0)$

$$S(q,c) = 1 - \frac{q^2\langle R_G^2\rangle}{3} - 2A_2Mc \tag{4}$$

Measurements of the excess Rayleigh ratio as a function of q and c allow calculation of M, $\langle R_G^2\rangle$, and A_2. In actual practice, the analysis of static light scattering data is more subtle. Additional issues are presented and discussed below.

A search of the literature for an absolute Rayleigh ratio for any liquid poses a problem, as there are no universally accepted values for $R^0(T,\lambda)$. We describe a reliable procedure for establishing a local standard for use in light scattering measurements, based on the existence of narrow molecular weight distribution polymers of well-accepted molecular weights.

While the Zimm limit is often assumed in measurements on dilute polymer solutions, the precision and range of validity are seldom discussed. The present article examines the full error analysis for light-scattering measurements on polymer solutions. Consideration of all the measured quantities necessary to determine M, $\langle R_G^2\rangle$, and A_2 are carried out. Recommendations for successful protocols are given and typical limits of error are established.

Dynamic light scattering is now considered routine[4]. The typical quantities obtained from this data are the average hydrodynamic radius $\langle R_h\rangle$ and the polydispersity index Q.

In the hydrodynamic limit $(q \to 0)$, the measured intermediate scattering function is

$$S(q,c,t) = S(q,c)\exp\left(-D_m q^2 t\right) \tag{5}$$

where $D_m(c)$ is the mutual-diffusion coefficient for the solution. For dilute solutions, the mutual-diffusion coefficient can be represented as

$$D_m(c) = D_0(1 + k_D c + \cdots) \tag{6}$$

The measured mutual-diffusion coefficient is then extrapolated to infinite dilution to obtain the single-particle, or self-diffusion coefficient:

$$D_0 = \frac{k_b T}{6\pi\eta R_h} \tag{7}$$

where η is the solvent viscosity. It can be shown that the diffusion virial coefficient is given by

$$k_D = 2A_2M - k_s - \bar{v} \tag{8}$$

where k_s is the virial coefficient for the friction coefficient for each chain and $\bar{v}$ is the partial specific volume of the polymer in solution.

For a polydisperse sample, the observed intermediate scattering function is not a single-exponential decay. The normalized relaxation function can be represented as

$$\phi(t) = \int_0^\infty G(\Gamma)\exp(-\Gamma t)\,d\Gamma \tag{9}$$

For the narrow distribution of relaxation rates associated with the present set of polymers, the cumulant expansion[5] of the relaxation function is most commonly employed

$$\ln\phi(t) = -\langle\Gamma\rangle t + \frac{\mu_2}{2}t^2 + \cdots \tag{10}$$

where the average relaxation rate $\langle\Gamma\rangle$ and the variance μ_2, given by

$$\mu_2 = \int_0^\infty (\Gamma - \langle\Gamma\rangle)^2 G(\Gamma)\,d\Gamma \tag{11}$$

are obtained from the initial slope and curvature of the logarithmic decay function. The so-called polydispersity index Q is the ratio $\mu_2/\langle\Gamma\rangle^2$ of the variance to the square of the average relaxation rate. The average hydrodynamic radius is then calculated as

$$\langle R_h\rangle = \frac{k_b T q^2}{6\pi\eta\langle\Gamma\rangle} \tag{12}$$

In the present article a full error analysis is carried out for the determination of the average hydrodynamic radius and the polydispersity index. If the actual molecular weight dependence of the single-particle diffusion coefficient is known, the polydispersity index can be related to the width of the distribution of molecular weights for the sample. Experimental details are discussed in an attempt to give a successful protocol for these measurements.

EXPERIMENTAL

Materials

Anionically polymerized polystyrene samples with molecular weights ranging from 3×10^3 to 2×10^6 were provided by Pressure Chemical Company (Pittsburgh, Penn.). The nominal molecular weights and lot numbers are listed in Table I. The polymers were dissolved in

TABLE I Summary of experimental results for polystyrene standards

Lot no.	Nominal M_W	Exp. M_W	A_2 (mol*cm^3/g^2)	D_0 (cm^2/s)	k_D cm^3/g	k_s cm^3/g	R_h (nm)	R_g (nm)	R_g/R_h	Q (range)
61213	3350	3350	1.26×10^{-3}	3.0×10^{-6}	0.78	6.71	1.3			0.08–0.13
50828	5780	6790	1.09×10^{-3}	2.31×10^{-6}	−3.5	17.4	1.7			0.03–0.10
30420	13,000	14,400	8.86×10^{-4}	1.52×10^{-6}	−7.6	32.2	2.6			0.05–0.08
30811	25,000	25,000	7.48×10^{-4}	1.15×10^{-6}	−3.92	40.4	3.4			0.03–0.05
80317	30,000	31,700	7.14×10^{-4}	8.54×10^{-7}	3.36	41.0	4.6			0.03–0.04
30908	50,000	45,100	5.80×10^{-4}	7.29×10^{-7}	11.3	40.1	5.4			0.04–0.05
61210	65,000	66,000	5.84×10^{-4}	6.19×10^{-7}	11.8	64.4	6.4			0.02–0.04
50522	90,000	95,200		4.66×10^{-7}	26.9	73.1	8.5			0.03–0.04
61126	116,000	106,000	4.99×10^{-4}							
50903	152,000	134,000	4.65×10^{-4}	3.91×10^{-7}	9.55	114	10.1	13.5	1.34	0.02–0.04
30126	170,000	181,000	4.44×10^{-4}	3.76×10^{-7}	29.8	191	10.5	14.2	1.35	0.01–0.05
50912	200,000	209,000	4.42×10^{-4}	3.38×10^{-7}	47.8	136	11.7	16.5	1.41	0.02–0.03
70114	290,000	274,000	3.95×10^{-4}	2.73×10^{-7}	43.8	172	14.5	20.0	1.38	0.01–0.04
61031	250,000	288,000	3.94×10^{-4}	2.81×10^{-7}	59.4	165	14.1	22.2	1.57	0.03–0.04
61120	650,000	597,000	3.52×10^{-4}	1.62×10^{-7}	153	375	24.4	32.0	1.31	0.02–0.09
80323	900,000	883,000	3.27×10^{-4}	1.28×10^{-7}	154	423	31.0	38.5	1.24	0.01–0.06
61111	2,000,000	2,020,000	2.50×10^{-4}	8.66×10^{-8}	273	662	45.7	65.4	1.43	0.04–0.08

HPLC-grade toluene and filtered through 0.2 μm Gelman Acrodisc filters directly into cylindrical light-scattering cells. Measurements were carried out at 25°C.

Light-Scattering Apparatus

The light-scattering setup consisted of a Spectra Physics model 2020 argon-ion laser operating at 514.5 nm. The polarization of the incident light was adjusted to be vertical with respect to the scattering plane. Scattered light was detected as a function of angle with a Brookhaven Instruments model BI-240 goniometer. The scattering angle could be measured to 1 minute of arc and could be reset with a vernier scale to the same precision. No uncertainty in the results should be attributed to a lack of precision in the determination of θ. Measurements were typically carried out over the range 30°–135°. Intensity measurements and correlation function calculations were carried out with a Brookhaven Instruments model BI-9000 correlator. Individual measurements were carried out until the root-mean-square error in the correlation function was better than 0.1%.

Light-Scattering Standard

The observed intensity for toluene depends on the temperature and wavelength, as it does for all liquids. The intensity also depends on the polarization of the incident and scattered light and on the interference filter used to isolate the scattered light. The scattered light was not analyzed for polarization in these measurements and the interference filter centered at 514.5 nm has a bandwidth of 8 nm. Toluene has substantial Raman scattering that will change the overall cross section unless it is excluded. The interference filter also excludes any fluorescence from the dissolved polymer. The temperature was regulated with a circulating water bath that kept the toluene-filled index-matching vat at a constant temperature.

There exists a sample of 110,000 MW polystyrene (Pressure Chemical, lot 4b) that has been extensively studied over the years. The uncertainty in the molecular weight of this sample is only 1%. Since the refractive increment for polystyrene in toluene is well known[1] ($dn/dc = 0.110 \pm 0.001$), the excess Rayleigh ratio can be calculated with an absolute precision of 3%. Equation (1) can then be used in reverse to obtain the absolute scattering cross section for toluene at $T = 298.15\,\mathrm{K}$ and $\lambda = 514.5\,\mathrm{nm}$;

$$R^{\circ}(298.15\,\mathrm{K}, 514.5\,\mathrm{nm}, \mathrm{toluene}) = (35 \pm 1) \times 10^{-6}\mathrm{cm}^{-1} \qquad (13)$$

Since the absolute Rayleigh ratio of toluene is known only to 3%, no molecular weight determined by light scattering can be any more accurate than this. All the other molecular weights reported in this article were determined relative to this value for toluene.

RESULTS AND DISCUSSION

Molecular Weights

Solutions were prepared such that the relative scattered intensity was in the range 2–4. Typically, three concentrations were studied. The count rate observed for the pure toluene could be adjusted by changing the incident laser intensity or by changing the scattering solid angle. Typical values for the digital photon count rate were in the range $\langle n \rangle = 50,000 \pm$ to one million counts/s. There is an intrinsic noise level associated with photon counting that scales as the square root of the count rate. For the count rates employed in this work, the statistical error is only 0.1–0.3%. This is much smaller than the absolute uncertainty associated with the standard. The count rate also depends on the scattering volume, which depends on the scattering angle as the reciprocal of $\sin\theta$.

For the lower molecular weights, the mean-square radius of gyration was small enough ($< 10^{-16}\,\mathrm{m}^2$) that the angular dependence of the excess Rayleigh ratio could be ignored. Measurements at several different low angles were averaged to yield an excess Rayleigh ratio for each concentration. The excess Rayleigh ratio in the thermodynamic limit can be expressed in the form

$$\frac{Kc}{\Delta R(c)} = \frac{1}{M}\left(1 + 2A_2Mc + 3A_3Mc^2 + \cdots\right) \qquad (14)$$

where A_3 is the osmotic third-virial coefficient. When the excess intensity is as large as that used to obtain good precision in the present work, the contribution of the third virial coefficient cannot be ignored. Yet, the contribution is also not large enough to obtain a reliable value of A_3 from experimental data alone. One common method employed for solvents like toluene is to evaluate the third virial coefficient in the good solvent limit:

$$A_3 = \frac{A_2^2 M}{3} \qquad (15)$$

Under these conditions, the right-hand side of Equation (14) depends only on M and A_2. This leads to a useful form for analysis of excess light-scattering data in good solvents proposed by Berry[7]:

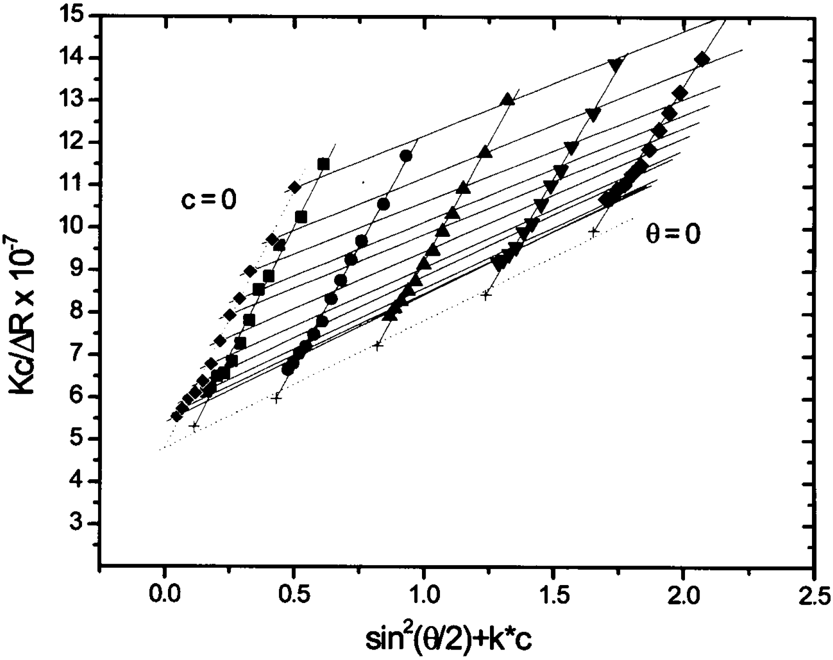

FIGURE 1 An example of a typical Zimm plot. Plot shown is for a polystyrene sample with $M_w = 2.02 \times 10^6$ and $k = 2000$.

$$\left[\frac{Kc}{\Delta R(c)}\right]^{1/2} = \left(\frac{1}{M}\right)^{1/2}(1 + A_2 Mc) \tag{16}$$

The values of $\Delta R(c)$ were then extrapolated to infinite dilution using Equation (16), and values of M and A_2 were obtained. The results are listed in Table I. For higher molecular weights, the excess Rayleigh ratios at each concentration were extrapolated to $q = 0$ and only then was Equation (16) employed. A typical plot of $(Kc/\Delta R)$ is shown in Figure 1. Weight-average molecular weights can be determined by light scattering with an accuracy of 3%, but the precision is closer to 1% due to photon statistics.

Osmotic Second Virial Coefficient

The osmotic second virial coefficients are shown as a function of molecular weight in Figure 2. Although they can be expressed empirically by a power law relation of the form

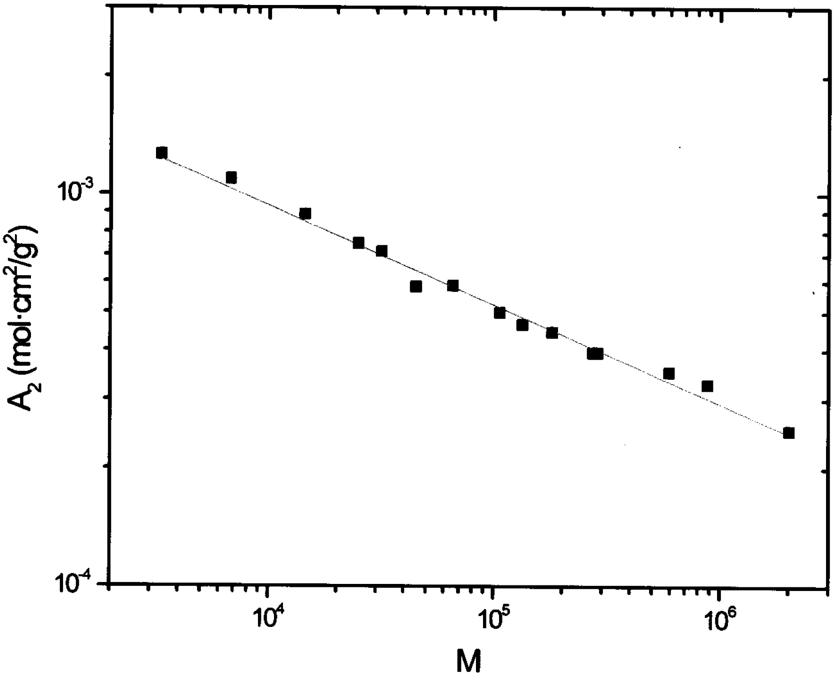

FIGURE 2 Molecular weight dependence of the osmotic second virial coefficient A_2 for polystyrene. The solid line indicates a power law fit to $A_2 = 9.50\times 10^{-3}\,M^{-0.25}$.

$$A_2 \cong KM^{-x}, \tag{17}$$

the intramolecular chain statistics are changing from the weak excluded volume regime at low M to the strong excluded volume regime at high M. The second virial coefficient can be expressed in terms of the excluded volume, u, of the chain as

$$A_2(M) = \frac{N_A u}{2M^2} \tag{18}$$

The excluded volume is defined in terms of the potential of the mean force between two polymer chains, $V(R)$, as

$$u = \int_0^{\infty}\left\{1 - \exp\left[-\frac{V(R)}{k_b T}\right]\right\}4\pi R^2 dR \tag{19}$$

In the limit of very low molecular weight, the excluded volume in a good solvent should increase with M, and the second virial coefficient should decrease very rapidly with increasing molecular weight. All polymers studied here are above this limit and behave more like random coils for $M > 3000$. In the random-coil limit without intramolecular excluded volume, the interchain excluded volume should increase as $M^{3/2}$ and the second virial coefficient should decrease as $M^{-1/2}$. As the chain length increases, the intramolecular excluded volume becomes more pronounced and the interchain excluded volume is expected to increase as $M^{3\nu}$, where the universal exponent for the chain expansion is approximately 0.6. Under these conditions, the osmotic second virial coefficient should decrease as $M^{-1/5}$[6]. A fit of all the results to a power law form yields an exponent of −0.25. The lowest molecular weight chains are not in the asymptotic limit for full excluded volume. For $M > 30{,}000$ a fit of the osmotic second virial coefficients conformed very well to an exponent of −0.20, in agreement with the theoretical expectation. Our results are also within experimental error of those compiled by Fetters et al.[3] Given the large range of the present data set and the good agreement with previous work, it should be preferable to treat the osmotic second virial coefficient as known as long as the nominal molecular weight is known to 10%. The empirical equation given in Figure 2 should yield accurate results over the entire range. This would allow the molecular weight to be determined under ideal routine conditions even from a single concentration.

Radii of Gyration

The mean-square radius of gyration can be reliably obtained only when the angular dependence of the structure factor S(q, c) exceeds at least three times the noise level. If the structure factor can be determined with 1% precision, the structure factor must change by at least 3% over the valid range for Zimm analysis. The root-mean-square radius of gyration is thus restricted to values in excess of 8.6 nm for the conditions in the present article. Even then, the precision of the measurement would only be 33%. In order to achieve a precision of at least 10%, the radius of gyration should exceed 15 nm. Values of $\langle R_G^2 \rangle$ are reported only for molecular weights that yield radii of gyration that exceed this value. Once the chain dimensions are sufficiently large to be reliably determined by light scattering, the question of the range of validity of the Zimm analysis arises. The scattering function for a random coil is given by the Debye function

$$S_D(u) = \left(\frac{2}{u^2}\right)[\exp(-u) - 1 + u] \tag{20}$$

where $u = q^2\langle R_G^2\rangle$. The Zimm limit agrees with the Debye function within 1% up to $u = 0.7$. This means that if the radius of gyration exceeds 23 nm, the Zimm limit will not be valid over the entire angular range. The use of Zimm analysis restricts the precision in the determination of the radius of gyration to 5%, since for $u = 0.7$ the scattering function will equal 0.8. Two approaches have been employed to improve the precision for larger chains. Berry noted that an expansion of the reciprocal of the square root of the scattering function is linear to much larger values of u[7]:

$$\left[\frac{1}{S_D(u)}\right]^{1/2} = 1 + \frac{u}{6} + \cdots \tag{21}$$

A comparison is shown in Figure 3. The Berry plot retains 1% precision up to $u = 2.7$. This approach extends the range of validity to radii as large as 45 nm.

If the polymer is known to be a random coil, the observed scattering function in the dilute range can be analyzed with the full expression

$$S(q, c) = S_D(q) S_{cm}(q, c) \tag{22}$$

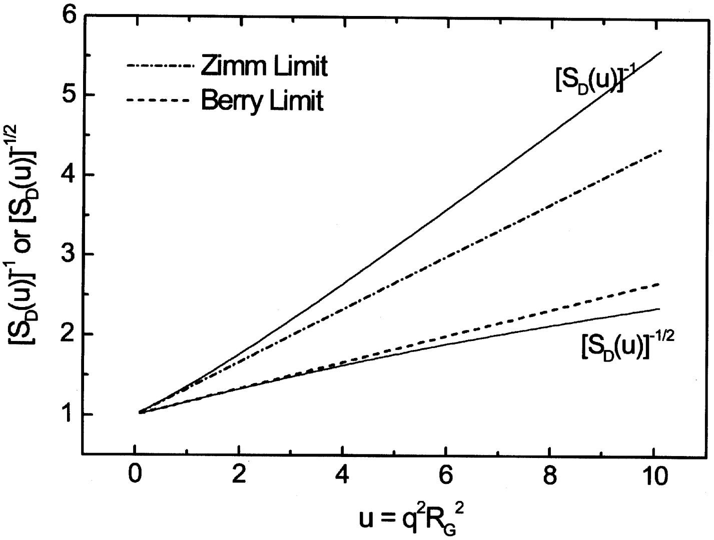

FIGURE 3 Comparison plot of Zimm and Berry approximations to the Debye function $S_D(u)$ for a random coil.

where the center-of-mass structure factor depends on both concentration and scattering angle. At the lower concentrations relevant for characterizing polymers in solution, a good approximation for the center-of-mass structure factor at finite values of q is

$$S(q,c)_{cm} = 1 - 2A_2McS_D(q) \tag{23}$$

While it is often assumed that there is no angular dependence in the intermolecular scattering function, it is clear from Equation (23) that at finite angles both thermodynamic and structural information is involved. Analysis of the full set of data for $S(q,c)$ then yields values for M, A_2, and $\langle R_G^2 \rangle$. Analysis of data obtained in dilute solution at even higher values of q and c has also been discussed in detail[8].

Values of the measured radii of gyration are plotted against $\log M$ in Figure 4. Only a single decade of molecular weight is available using the criterion articulated above. Measurement of the scattering function using light scattering for chains with molecular weight in excess of two million is not routine. Special care is needed to prepare optically perfect solutions of high molecular weight chains without degradation. The present results can be represented empirically as:

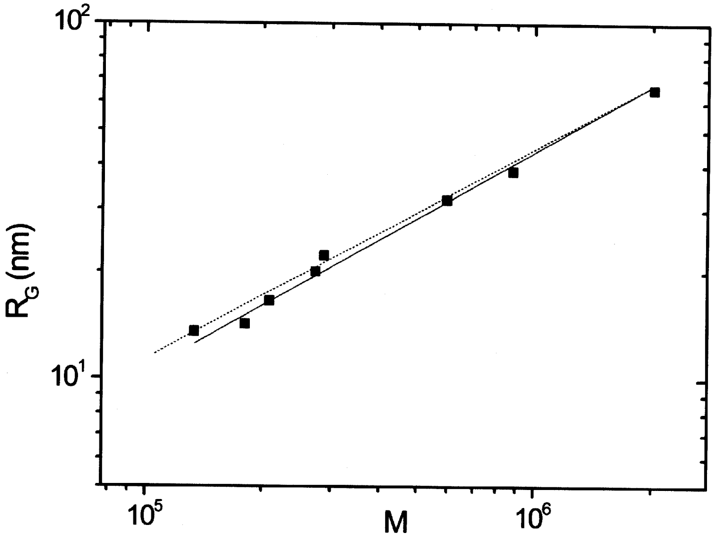

FIGURE 4 Molecular weight dependence of the radius of gyration R_G for polystyrene. The solid line indicates a power law fit to $R_G = 8.1 \times 10^{-3} M^{0.62}$. The dashed line represents results obtained by Fetters, et al.[3].

$$R_G = 8.1 \times 10^{-3} M^{0.62} \tag{24}$$

The present results are also compared to literature results in Figure 4. Good agreement is obtained over the common range.

For a random coil polymer in a good solvent, the radius of gyration is expected to increase as M^{ν}. The present results are within experimental error of the theoretical expectation, but the limited precision of the data and the limited range of M lead to substantial uncertainty in the value of the exponent.

Mutual-Diffusion Coefficient

Mutual-diffusion coefficients were measured for each sample as a function of molecular weight using the definition

$$D_m(c) = \lim_{q \to 0} \frac{\langle \Gamma \rangle}{q^2} \tag{25}$$

The results were analyzed using Equation (6) to yield the self-diffusion coefficient, D_0, and the virial coefficient, k_D. The values are listed in Table I. Since the values of the second virial coefficient and the partial specific volume of polystyrene are known, the frictional virial coefficients can be calculated. The results are also listed in Table I.

The self-diffusion coefficients are plotted against molecular weight in Figure 5. They can be represented empirically as

$$D_0(M) = 2.8 \times 10^{-4} M^{-0.55} \tag{26}$$

If the infinite dilution limit of the mutual-diffusion coefficient can be measured, the molecular weight can be determined quite accurately from this formula over the range 3,000 to two million.

The diffusion coefficients can also be converted to a hydrodynamic radius using Equation (7). The results are listed in Table I and presented in Figure 6. Because the lowest molecular weight chains are not in the asymptotic limit for hydrodynamic interaction, the empirical molecular weight dependence calculated from the hydrodynamic radii is not just the reciprocal of the self-diffusion coefficient. The empirical result is

$$R_h = 9.12 \times 10^{-3} M^{0.59} \tag{27}$$

The present results for the hydrodynamic radius are also compared to data compiled by Fetters et al.[3] in Figure 6. All the data is well represented by Equation (27). The molecular weight exponent is within experimental error of the scaling exponent ν. While dynamic scaling is not as well established as static scaling, the results are satisfying.

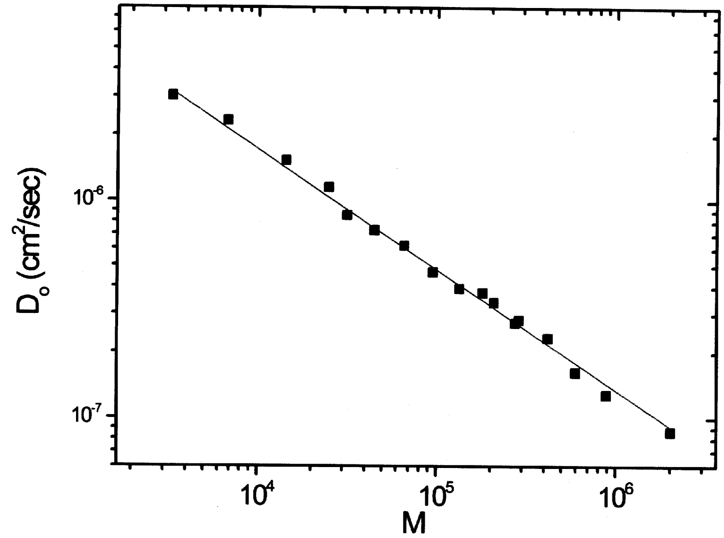

FIGURE 5 Molecular weight dependence of the self-diffusion coefficient D_o for polystyrene. The solid line indicates a power law fit to $D_0 = 2.80 \times 10^{-4} M^{-0.55}$.

The calculated values of the diffusion virial coefficient are plotted against $\log M$ in Figure 7. For the lowest molecular weights, the value of k_D is dominated by the partial specific volume contribution and hence is negative. At the highest molecular weights the virial coefficient is increasing rapidly, as $2A_2M$ dominates the value. The values of k_D are known well enough that if the nominal molecular weight is known, the self-diffusion coefficient could be reliably calculated from a single concentration measurement of the mutual-diffusion coefficient. Since both the osmotic contribution and the density contribution are known with good precision, the frictional virial coefficient can also be calculated without significant loss of precision. The values are plotted against M in Figure 8. The data can be represented in power law form as

$$k_S(M) = 5.82 \times 10^{-2} M^{0.65} \tag{28}$$

Polydispersity Index

Dynamic light scattering provides a useful tool for determining the width of the distribution of molecular weights for atactic polystyrene samples, but there is typically confusion when comparing the polydispersity Q from the experimental relaxation function and the polydispersity M_w/M_n in molecular weight. The purpose of this section is to

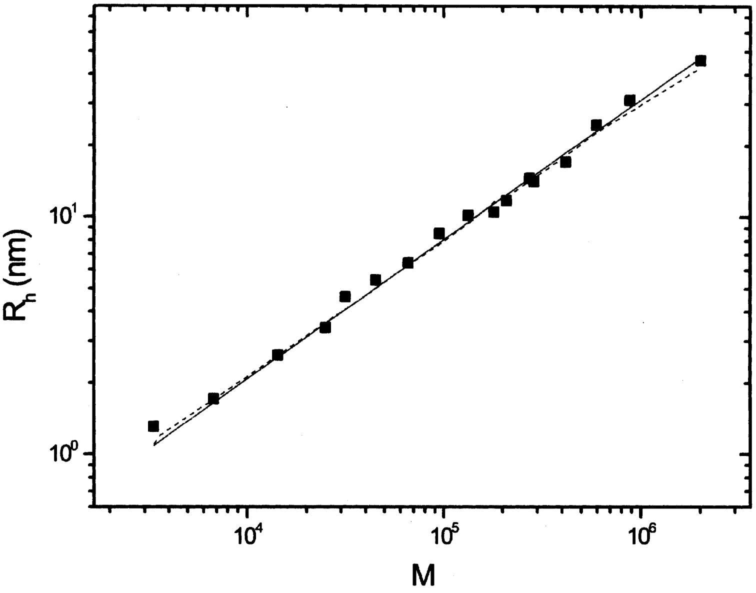

FIGURE 6 Molecular weight dependence of the hydrodynamic radius R_h for polystyrene. The solid line indicates a power law fit to $R_h = 9.12 \times 10^{-3} M^{0.59}$. The dashed line represents results obtained by Fetters et al.[3].

calculate and compare both quantities starting from a particular shape of the molecular weight distribution. Two types of distribution functions will be considered here.

The intermediate scattering function for a mixture of molecular weights can be represented as

$$S(q,t) = \sum_i \left[\frac{\rho(M_i) M_i^2}{\sum_i \rho(M_i) M_i^2} \right] S_i(q) \exp\left[-\frac{k_b T q^2 t}{6\pi\eta R_h(M_i)} \right] \qquad (29)$$

where $\rho(M_i)$ is the probability of having a molecular weight of M_i. The function $S(q, t)$ is calculated numerically at 25 °C over the same time range used in a typical experiment, with R_g and R_h given by Equations (24) and (27), respectively. The calculated scattering function is truncated at a point such that the function has clearly reached the baseline, typically after three decades of decay, and is analyzed using a cumulant expansion; see Equation (10).

An ideal anionic polymerization yields a Poisson distribution of molecular weights

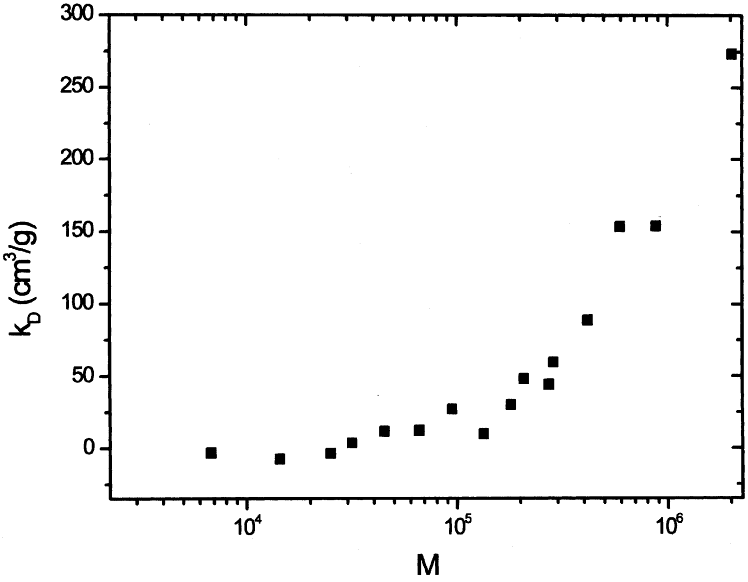

FIGURE 7 Calculated values for the diffusion virial coefficient k_D for polystyrene.

$$\rho(M) = \frac{\exp\left[-\left(\frac{\langle M\rangle}{m} - 1\right)\right]\left(\frac{\langle M\rangle}{m} - 1\right)^{\left(\frac{M}{m}-1\right)}}{\left(\frac{M}{m} - 1\right)!} \tag{30}$$

where m is the molar mass of the monomer unit. The ratio of the weight-to-number average molecular weight for such a distribution is given by

$$\frac{\langle M\rangle_w}{\langle M\rangle} = 1 + \frac{\frac{\langle M\rangle}{m} - 1}{\left(\frac{\langle M\rangle}{m}\right)^2} \tag{31}$$

Values of Q were calculated for degrees of polymerization of 10, 100, and 1000 and are listed in Table II along with the weight-to-number average ratio. The calculated values of Q, with decreasing M, are between 0.0004 and 0.02 for the three molecular weights. While an ideal anionic polymerization approaches a Poisson distribution, real commercial samples have a broader molecular weight distribution.

Another distribution function for moderately narrow distributions is a lognormal distribution of molecular weights:

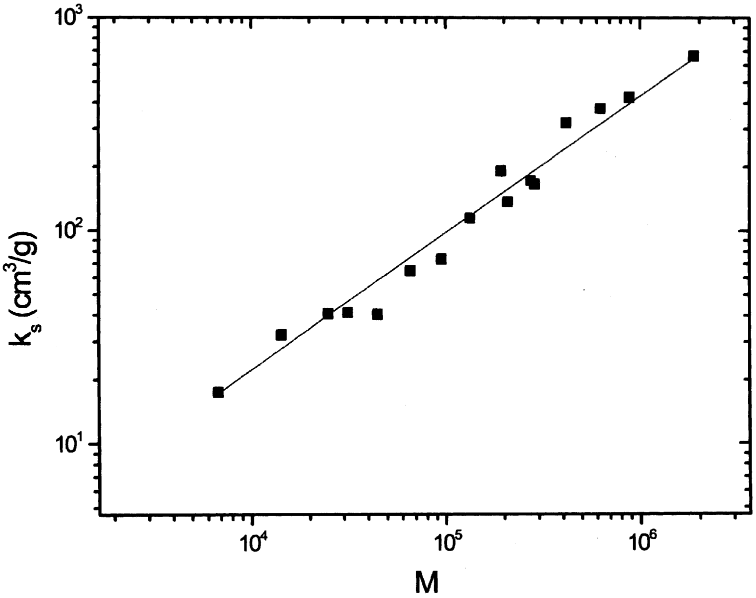

FIGURE 8 Calculated values for the frictional virial coefficient k_s for polystyrene. The solid line indicates a power law fit to $k_s = 5.82 \times 10^{-2} M^{0.65}$.

$$\rho(M) = \left(\frac{\langle M\rangle}{M\beta\sqrt{2\pi}}\right)\exp\left\{-\frac{\left[\ln\left(\frac{M}{\langle M\rangle}\right)\right]^2}{2\beta^2}\right\} \qquad (32)$$

The weight-to-number average ratio for this distribution depends only on the width parameter β

$$\frac{\langle M\rangle_w}{\langle M\rangle} = \exp\left(\frac{\beta^2}{2}\right) \qquad (33)$$

Values of Q were calculated for a lognormal distribution as a function of the weight-to-number average ratio. Because there is a high molecular weight tail associated with this distribution, the results depend on the scattering vector for broad distributions. Each molecular weight contributes in proportion to the value of its scattering function $S(q)$, which causes the scattering by larger chains to be strongly attenuated at higher angles.

Comparison of the Q values obtained from the two distribution functions is shown in Figure 9. The values calculated are at a scattering

TABLE II Comparison of the calculated polydispersity indices Q for a Poisson distribution of chain lengths and the experimental Q values for some samples with comparable molecular weights.

Poisson Distribution				
DP_n	DP_w	M_w	M_w/M_n	Q (theoretical)
10	~12	1250	1.09	0.018
100	~102	10,600	1.01	0.002
1000	~1004	104,400	1.00	0.0004
Experimental Results				
	DP_w	M_w	M_w/M_n[a] (lognormal)	Q (experimental)
	~30	3350	1.35	0.08
	~140	14,400	1.16	0.05
	~920	95,200	1.10	0.03

[a] Taken from Figure 9, assuming a lognormal distribution of molecular weights.

angle of 30°, and the lognormal distribution has a number average degree of polymerization of 100. Typical Q values between 0.02 and 0.06 correspond to M_w/M_n values between 1.05 and 1.2 for the lognormal distribution. These values are closer to the M_w/M_n values, below 1.1, quoted by the vendor for samples with a molecular weight around 10^4 g/mol.

Some of the experimental Q values are slightly higher than those calculated in either distribution, for M_w/M_n values below 1.1, especially when comparing the experimental results to those obtained from the Poisson distribution (Table II). Although it is easy to calculate Q from a calculated intermediate scattering function of arbitrary precision on a computer, obtaining precise values for Q is difficult in the laboratory. The second cumulant depends on the curvature of the decay in a logarithmic plot. The actual data points contain noise at all values of the decay time. At the shortest decay times, the signal-to-noise ratios are lower because the small number of photons that arrive during the short time interval necessary to calculate the correlation function for small decay times limits the statistical averaging. At the longest decay times, the correlation function is nearing the baseline and the noise is comparable to the value of the difference between the observed intensity correlation function and the calculated baseline value. In order to accurately

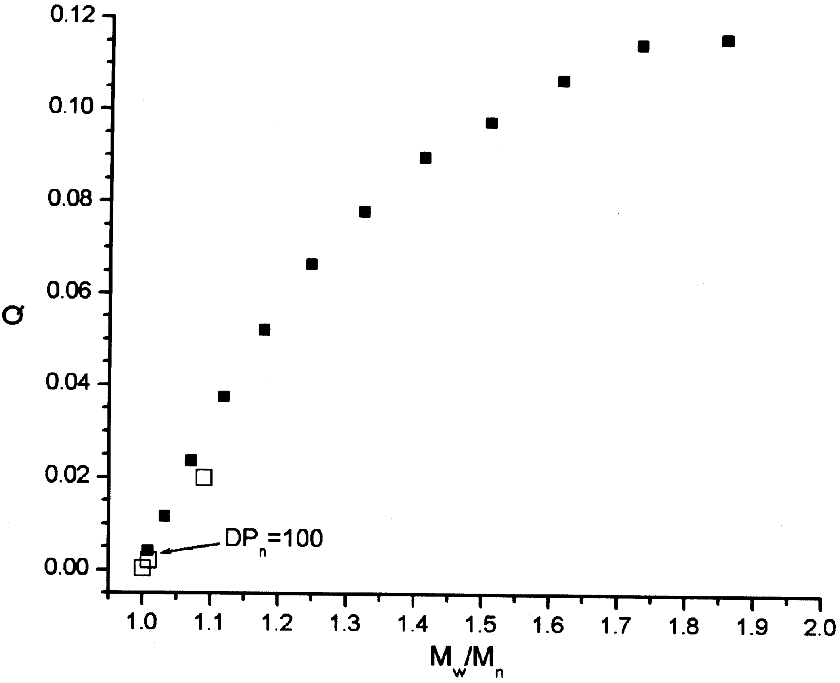

FIGURE 9 Predicted values of the polydispersity index Q for various M_w/M_n ratios. The open points were obtained using a Poisson distribution centered at $DP_n = 10$, 100, and 1000. The solid points were calculated using a lognormal distribution of chain lengths, centered at $DP_n = 100$, at a scattering angle of 30°.

determine the curvature, at least three decades of logarithmic decay are useful, and the fit must be carried out to a fourth-order polynomial. To obtain data good enough to adopt these stringent criteria, long averaging times are required. Realistically, a polydispersity of 0.005 is very close to the limit of what can be obtained reliably.

While it might be thought that better results would be obtained by increasing the scattered intensity through a larger scattering volume, larger scattering volumes lead to a distribution of q values for the observed light. In order to assess the effect of the scattering solid angle on the measured value of Q, a solution of $M = 181{,}000$ polystyrene was prepared and studied at a scattering angle of 30°. A concentration around 2 mg/mL was chosen to give an excess scattering twice as large as the solvent intensity, and data were collected for 10 minute durations. The scattering solid angle was adjusted by changing the diameter of the defining pinhole in the observation optical train.

The quantity actually computed in most dynamic light-scattering experiments is the intensity autocorrelation function:

$$g^{(2)}(q,\tau) = \frac{\langle I(q,0)I(q,\tau)\rangle}{\langle I(q)\rangle^2} \tag{34}$$

For a Gaussian random signal, the intensity autocorrelation can be related to the desired field autocorrelation function by

$$g^{(2)}(q,\tau) = 1 + f(A)\left[g^{(1)}(q,\tau)\right]^2 \tag{35}$$

where A is called the coherence area and the function $f(A)$ depends explicitly on the scattering solid angle. For small coherence areas $f(A) = 1$, but the scattered intensity is very low under these conditions. An optimal value of A is chosen where $f(A)$ is still near 1, but the intensity is high enough to obtain well-averaged data in a reasonable time. Another effect of larger coherence areas is the explicit q dependence of the decay rate. A distribution of q values increases the width of the distribution of observed decay rates, although the average decay rate remains the same. For an optimal value of the observation pinhole in our spectrometer (200 μm), the function $f(A)$ exceeds 0.9, and the distribution of observed scattering vectors is narrow enough to contribute no measurable increase in Q. At smaller pinhole diameters, the decrease in intensity requires inordinately long averaging times to obtain good signal-to-noise ratios. At comparable averaging times, the apparent value of Q increases due to noise in the correlation function. At 800 μm, the calculated value of Q is measurably larger than at 200 μm, and for larger scattering solid angles, the observed value of Q can easily be 10 times the value observed at 200 μm. For this experimental sample, the lowest value of Q was 0.008. This corresponds to a weight-to-number average ratio of 1.03, which is comparable to that claimed by the vendor for this sample.

If sufficient effort is expended, dynamic light scattering can be a useful tool in the study of the width of the distribution of molecular weight for anionically polymerized polystyrene samples; however, care is necessary to minimize errors in the correlation function that could contribute to an increase in Q. It should not be assumed that the value of Q obtained under conditions normally employed to measure the mutual-diffusion coefficient is an accurate measure of the molecular weight distribution for the sample.

CONCLUSIONS

A series of anionically polymerized polystyrene samples, ranging in molecular weight from 3×10^3 to 2×10^6, were characterized in dilute solution with toluene. The power law dependences on molecular weight of R_g, D_0, R_h, and k_s were determined. A comparison of measured polydispersity indexes with those derived from two types of molecular weight distributions found that with very careful control of the experiment it is possible to obtain a reasonable value for the weight-to-number average value for the sample, assuming a particular shape of the distribution.

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