Dynamics of Flexible Coils in an Isorefractive Rod/Coil Composite Liquid. 1. Binary Polystyrene/Solvent Solutions

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ABSTRACT: Dynamic light scattering (DLS) and static light scattering (SLS) were used to characterize the structure and dynamics of solutions of polystyrene of molecular weight 390 000 in 1,1,2,2-tetrachloroethane. Mutual diffusion coefficients were determined as functions of concentration and temperature. The diffusion virial coefficients were determined and compared to several theoretical predictions. The DLS intensity autocorrelation function was also carefully examined for the possible presence of fast modes in order to provide a comparison to polystyrene studied in ternary solutions including a rodlike polymer (paper 2).

I. Introduction

The diffusion of polystyrene in dilute solution is a problem that has been examined by numerous authors. The major purpose of this study is to develop a more thorough understanding of the dilute solution behavior of polystyrene in order to interpret results found in more complicated ternary solutions.[1] A number of studies have detailed the effects of polymer concentration on the polymer mutual diffusion coefficient, D.[2-14] D is described by a linear dependence on the mass concentration, c, through a diffusion virial coefficient, k_D (also called the concentration coefficient),

$$D = D_0(1 + k_D c + ...) \qquad (1)$$

where D_0 is the mutual diffusion coefficient at infinite dilution. The diffusion coefficient can also be expressed with a dependence on volume fraction, c_v, instead of mass concentration. The equation describing this is of the same form as eq 1,

$$D = D_0(1 + k_{D,v} c_v + ...) \qquad (2)$$

where $k_{D,v}$ is the corresponding virial coefficient when the concentration is given in terms of volume fraction. The volume fraction can be related to the mass concentration if the hydrodynamic volume of the polymer is known. The equation describing this dependence is

$$c_v = \left(\frac{4\pi N_A R_H^{\,3}}{3M}\right)c \qquad (3)$$

where R_H is the hydrodynamic radius of the polymer.

Although significant progress has been made toward understanding this effect, a more complete understanding is desirable. In this work we present experimental results for the concentration dependence of the diffusion coefficient of polystyrene in a good solvent. These results (along with a compilation of previous experimental data collected by other authors) are compared to the predictions of several theories of the diffusion virial coefficient of polymer coils.

II. Experimental Section

Sample Preparation. The polystyrene was purchased from Pressure Chemical Corp. with stated molecular weight 390 000, $M_W/M_n < 1.10$, Lot No. 3b. The 1,1,2,2-tetrachloroethane was 99% grade supplied by Aldrich and used without further purification.

The samples were filtered using Millipore 0.2 μm pore size, 13 mm diameter GS filters for the DLS measurements. Two filters were used in each stainless steel Swinnex holder, and Teflon gaskets and O-rings were used in all cases. The light scattering measurements were made in 1 cm square pyrex fluorimeter cells with Teflon-linked screw cap lids (Spectrocell RF-1010-T).

Sample preparation was as follows. The cells were cleaned overnight in a chromic acid solution. They were rinsed with deionized, distilled water and then with acetone and subsequently dried. They were then repeatedly rinsed with filtered solvent. The cell was checked for dust contamination by passing a 200 mW, 488 nm laser beam through the solvent-filled cell and viewing the beam at an angle of 90° and at 5× magnification. Dust particles (i.e., millimeter-sized impurities[15]) appear as bright specks under these conditions.

The same filters used to clean the cell were used for the sample filtration. Approximately 1 mL of solution was allowed to displace the volume of solvent remaining in the filter holder. The cleaned cells were then emptied and rinsed with ~1 mL of filtered solution to remove the remaining solvent on the cell walls. The remaining solution (~2 mL) was then introduced into the cell for light scattering measurements. The cell threads were lined with Teflon tape to ensure a tight seal and prevent evaporation.

Dynamic Light Scattering. The dynamic light scattering (DLS) apparatus used has been described in detail elsewhere.[16] The static light scattering (SLS) apparatus used is a modification of an apparatus designed and constructed in our laboratory by Lewis and described elsewhere.[17,18]

Analysis of the autocorrelation functions from DLS was performed using the standard data analysis program CONTIN.[19-22] The autocorrelation function for a system of polydisperse particles can be represented as a sum of many exponential decays

$$g^{(1)}(t) = \int_0^\infty x(\Gamma)\exp(-\Gamma t)\,d\Gamma \qquad (4)$$

where Γ is the decay constant (relaxation frequency) and $x(\Gamma)$ is the fraction of scattered intensity contributed by particles with decay constant Γ. For a monodisperse dilute solution of spherical particles $x(\Gamma)$ is a delta function with the nonzero value of x at $\Gamma = q^2D$. In general, there are particles of different size and/or shape contributing to the autocorrelation function. The problem is to determine the form of $x(\Gamma)$ from the measured DLS time correlation functions. Non-single-exponential correlation functions can also arise from contributions of molecular rotational and flexing modes of motion and, in nondilute solutions, from intermolecular interactions.

Solutions generated by CONTIN were chosen with the Fisher statistic (Prob. 1 to reject) between 0.2 and 0.5. When the solution changed with the degree of smoothing, then each solution had to be considered as possibly correct. Generally, however, the solutions were essentially identical over a wide range of smoothing, particularly when the data were of high quality.

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In the attempt to resolve fast relaxations of low amplitude in the correlation function, it was necessary to consider the effects of both photomultiplier tube (PMT) afterpulsing and "artifacts" in the CONTIN fitting process. For very short time scales one has to consider the effects of photomultiplier tube afterpulsing, which results from correlated events in the operation of the PMT. Afterpulsing is most significant in the first microsecond of a correlation spectrum, although it can extend as far as 3 ms for the PM tubes used for these experiments. The physical effect causing this correlated behavior has been described elsewhere.[23,24]

In the context of a DLS experiment these correlated events can obscure relaxation processes occurring on similar time scales. Certain experimental methods have been developed to remove this process, but these are generally complicated (e.g., cross correlation,[25] time-of-arrival spectroscopy,[26,27] etc.). With regard to the data presented here, it is important to be aware of the effects of afterpulsing, but it is not necessary to physically remove it.

In all correlation functions analyzed in this work the first data point was discarded. In most cases this was sufficient to remove any effect of afterpulsing. In general, the fastest relaxation time that may be reliably observed can be determined from the delay time chosen in the DLS experiment. For example, if a delay time of 10 ms is chosen, then no information is obtained on relaxations that decay entirely within the first 10 ms (assuming that the first data point is discarded).

As well as afterpulsing, there has been concern about artifacts in the CONTIN fitting process.[28] These artifacts are fast relaxation processes reported by CONTIN which marginally improve the CONTIN fit but are suspected to be physically unfounded. Typically these are of very low amplitude and large error (>100%). Another characteristic is that they appear as the fastest relaxation possible given the fixed lower limit of integration used in a particular CONTIN analysis. If one expands the limits of integration to include faster relaxations, then the location of the peaks due to the artifacts typically follows the limit of integration. The presence of a fast relaxation was discarded when it would represent a process that had entirely decayed during the first sample time, since the first sample time was always discarded.

Static Light Scattering. Static light scattering (SLS) was used to measure the radius of gyration, the thermodynamic second virial coefficient, and the molecular weight of the polystyrene. The intensity of the scattered light from a polymer solution is given by the equation[29]

$$\frac{K^*c}{R_\theta} = \frac{1}{M_w}\left[1 + \frac{16\pi^2}{3\lambda^2}R_G^{\,2}\sin^2(\theta/2)\right] + 2A_2c + \ldots \qquad (5)$$

where R_θ is the Rayleigh ratio, λ is the wavelength of incident radiation in vacuo, and R_G^2 is the mean square radius of gyration. For vertically polarized incident radiation, the optical constant, K^*, is given by

$$K^* = \frac{4\pi^2 n^2 (dn/dc)^2}{\lambda^4 N_A} \qquad (6)$$

where n is the index of refraction of the solvent and dn/dc is the differential index of refraction. Zimm plots were constructed in order to extrapolate to both zero angle and concentration in eq 5.

Differential Index of Refraction. A Brice-Phoenix differential refractometer was used to determine the differential refractive index, dn/dc, which is also referred to as the specific refractive index increment, ν. This was calibrated using aqueous NaCl solutions.[30] All values of ν were measured at both 436 and 546 nm. The value at 488 nm was determined by linear interpolation. In all cases the error in the 436 and 546 nm values was nearly as large as the difference between the values, so the method of interpolation was not critical.

Polystyrene samples with concentrations of 5.0, 7.5, and 10.0 mg/mL were used for differential refractometry. These provided greater refractive index differences from solvent, thus allowing a more precise determination than was possible using the concentrations studied with DLS. These were still well within the dilute range, and there was no indication of nonlinear behavior in the concentration dependence. In addition, the sample cell was oriented to maximize refraction of the incident beam. The concentration was adjusted due to the changing temperature. This is necessary because the solution concentration was initially determined at room temperature. The solution expands upon heating, but the mass of polymer does not change, so that the mass concentration decreases with increasing temperature. The solvent density was used to determine the expansion of the solution. A constant temperature bath was used to circulate water through the cell block for temperature control. The addition of foam insulation around the cell block was necessary for measurements made at 75.0 °C. For the temperatures 25, 50, and 75 °C the respective values of ν were 0.122, 0.124, and 0.127 ± 0.001 mL/mg.

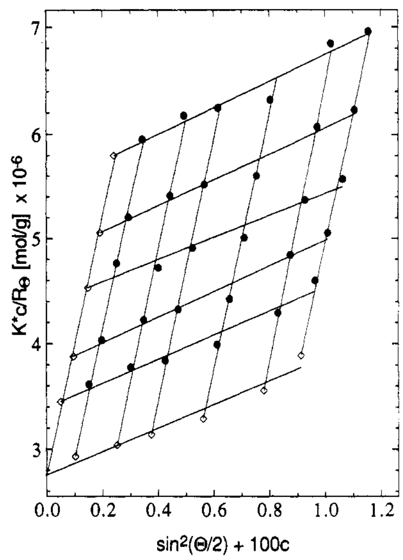

Figure 1. Zimm plot for polystyrene, MW = 390 000 in 1,1,2,2-tetrachloroethane at a temperature of 50.0 °C: (●) experimental data; (◇) extrapolation to zero angle and concentration.

III. Results and Discussion

Molecular Weight, Radius of Gyration, and Thermodynamic Virial Coefficient. All static parameters were determined from SLS using Zimm plots. A representative Zimm plot is shown in Figure 1. Experiments were performed at 25.0, 50.0, and 75.0 °C. The radii of gyration obtained are respectively 31.0 ± 1.7, 31.2 ± 1.4, and 30.2 ± 1.8 nm. The second virial coefficients, A_2, are respectively 7.0 (±0.1) × 10^{-4}, 6.2 (±0.2) × 10^{-4}, and 5.9 (±0.1) × 10^{-4} mol·cm^3·gm^{-2}. The molecular weight determined from the Zimm plots varied between 370 000 and 420 000 in agreement with the nominal molecular weight of 390 000 given by the manufacturer.

Concentration Dependence of Diffusion Coefficient. Five samples were prepared with the following concentrations at 20 °C: 0.5, 1.0, 1.5, 2.0, and 2.5 mg/mL. For a flexible coil one may define an overlap concentration, the concentration at which the coils begin to interpenetrate each other, c^*, as

$$c^* = M/N_A R_G^{\,3} \qquad (7)$$

For molecular weight 390 000 and radius of gyration 30 nm, the overlap concentration is 24.0 mg/mL. Below c^* the solution may be considered dilute and effects due to concentration can be handled using virial expansions. The concentrations studied here are, using this criterion, in the dilute regime.

The mutual diffusion coefficient, D, was measured for these samples between the temperatures of 20.0 and 75.0

Table 1. Diffusion Coefficients ($\times 10^8$ cm^2/s)

	concentration (mg/mL)				
temp (°C)	0.5	1.0	1.5	2.0	2.5
20	6.99	7.38	7.67	8.01	8.29
25	7.90	8.19	8.37	8.69	9.15
30	8.67	9.12	9.29	9.74	10.22
35	9.41	9.87	10.21	10.73	11.05
40	10.17	10.86	11.36	11.72	12.37
45	11.17	11.83	12.27	12.83	13.25
50	12.43	12.90	13.36	13.81	14.41
55	13.18	13.86	14.45	14.91	15.77
60	14.21	14.86	15.70	16.07	16.79
65	15.63	16.00	16.68	17.32	18.01
70	16.65	17.45	18.49	18.84	20.00
75	17.91	18.60	19.82	20.34	20.85

Table 2. Polystyrene, MW = 390K, in TCE

temp (°C)	$D_0 \times 10^8$ (cm^2/s)	k_D (mL/g)	k_D (unitless)
20	6.70	96.2	2.39
25	7.55	82.2	2.19
30	8.30	90.4	2.37
35	9.02	93.0	2.38
40	9.72	110.1	2.72
45	10.73	98.5	2.57
50	11.93	89.1	2.55
55	12.57	102.3	2.62
60	13.62	97.0	2.61
65	14.75	92.2	2.50
70	15.91	100.6	2.78
75	17.22	93.2	2.63

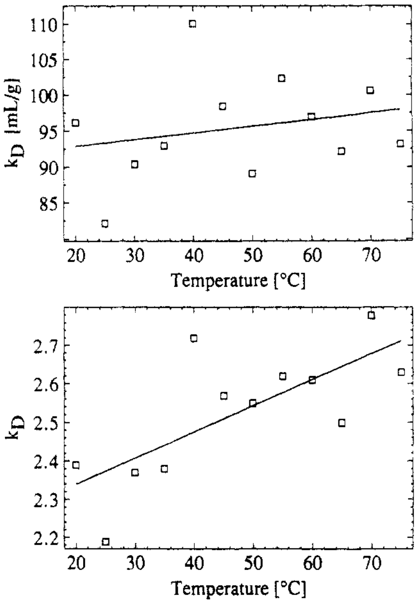

Figure 2. Concentration virial coefficient, k_D, as a function of temperature: (a) k_D in units of mL/g; (b) dimensionless k_D.

Table 3. Density and Solvent Values for TCE; Hydrodynamic Radius of PS, MW = 390K, in TCE

temp (°C)	density (g/mL)	viscosity (cP)	hydrodyn radius (nm)
20	1.597	1.74	18.41
25	1.589	1.61	17.96
30	1.582	1.48	18.07
35	1.574	1.37	18.20
40	1.566	1.28	18.43
45	1.558	1.20	18.09
50	1.550	1.13	17.55
55	1.543	1.05	18.20
60	1.535	1.00	17.91
65	1.527	0.94	17.86
70	1.519	0.89	17.74
75	1.512	0.84	17.62

°C (in 5 °C increments) using DLS. The measured diffusion coefficient increased with increasing concentration. At all temperatures the increase in the diffusion coefficient showed a linear dependence on concentration. The values are shown in Table 1. Each individual diffusion coefficient was determined by a linear fit to a plot of the relaxation constant, Γ, as a function of q^2, where q is the scattering vector.

The measured value of k_D varied between 80 and 110 mL/g with changing temperature. The results are shown in Table 2. The value of k_D was slightly dependent on temperature, showing an increase with increasing temperature (see Figure 2a). This is to be expected if the solvent quality increases with increasing temperature.

The hydrodynamic radius must be measured to determine $k_{D,v}$ (see eqs 2 and 3). The hydrodynamic radius is defined using the Stokes–Einstein relation,

$$R_H = \frac{k_B T}{6\pi\eta D_0} \tag{8}$$

where k_B is Boltzmann's constant, T is absolute temperature, and η is the viscosity of the solvent. An independent measure of the viscosity is necessary in order to determine R_H. The kinematic viscosity of the solvent was measured at temperatures of 20.0–75.0 °C in 5 °C increments using a Cannon-Ubbelohde (size 50) viscometer. The measured times were always greater than 150 s, so that no kinetic energy correction was necessary. Other corrections (e.g., buoyancy, surface tension, etc.) were also determined to be negligible.[31] The kinematic viscosity was related to the dynamic viscosity (the value typically reported as the "viscosity") by the solution density. The calculated hydrodynamic radii were between 17.5 and 18.5 nm. They were essentially temperature independent, although a slight decrease in size with increasing temperature may have been masked by the error, which was ~1% (Table 3).

The value of $k_{D,v}$ ranged from 2.19 to 2.78 and again showed a slight increase with temperature (Table 2 and Figure 2b). Both coefficients will be subsequently referred to as k_D in keeping with standard practice.

Theoretical Predictions for the Concentration Dependence of Diffusion Coefficients. The dependence of the diffusion coefficient, D, on concentration has been theoretically calculated by several authors.[3-9] The diffusion coefficient can be related to both thermodynamic and hydrodynamic factors using a derivation based on the Gibbs–Duhem equation which leads to the result

$$D = \frac{k_B T}{f}\left(1 - \frac{N_A v_1}{M}c\right)(1 + 2A_2 M c + ...) \tag{9}$$

where f is the friction coefficient, v_1 the partial specific volume of the polymer, M the molecular weight, and A_2 the thermodynamic second virial coefficient. This can be compared to the experimentally determined values of k_D, by calculating the contributions to D from both thermodynamic and hydrodynamic factors. The hydrodynamic contribution is obtained in the concentration dependence of the friction coefficient. The thermodynamic contribution appears in the thermodynamic second virial coefficient.

The thermodynamic part of k_D is often expressed in terms of an effective hard-sphere radius, S, which is defined as

$$S = \left(\frac{3M^2 A_2}{16\pi N_A}\right)^{1/3} \tag{10}$$

and is generally referred to through the parameter $X \equiv$

Table 4. Polystyrene, MW = 390K, in TCE; Static Light Scattering Results

temp (°C)	R_H (nm)	R_G (nm)	R_H/R_G	S/R_H	$A_2 \times 10^4$ (mol·cm³/g²)	S/R_H
25	18.2	31.0	0.5871 ± 0.027	1.25 ± 0.2	7.0	1.21 ± 0.02
50	18.0	31.2	0.5769 ± 0.048	1.35 ± 0.4	6.2	1.17 ± 0.03
75	17.7	30.2	0.5861 ± 0.036	1.25 ± 0.3	5.9	1.17 ± 0.02

S/R_H. The ratio R_H/R_G can be used to determine the value of the hard-sphere radius, S, of the coil using the theory of Akcasu.[6] In the Akcasu theory, if $R_H/R_G \approx 0.58$, then $S/R_H \approx 1.3$. One can also use the second virial coefficient to determine the hard-sphere radius from eq 10.[3] Values of S/R_H determined by both methods are shown in Table 4. The values found using the second virial coefficient, although slightly lower, agree with those found from R_H/R_G and the Akcasu theory. The limiting values of R_H/R_G in the Akcasu theory are a minimum of 0.537 in good solvent and a maximum of 0.664 in Θ solvent. The measured ratios indicate that tetrachloroethane is closer to a good solvent than to a Θ solvent. There is no measurable change with increasing temperature, which indicates that the solvent quality does not change much at these temperatures.

The decrease in the virial coefficient predicts a slight decrease in S (i.e., a worsening of solvent quality) which is not expected. This trend, however, is also of the same size as the experimental variation. It seems safest to assume that the solvent quality only changes slightly, if at all, with temperature. This is also an indicator of good solvent quality, since a poor solvent would be expected to become significantly better with increasing temperature.

Although there is considerable agreement of some of the theoretical predictions with experiment in Θ solvent conditions, the agreement is not as good for good solvent conditions. In particular, the good solvent data in the literature show a lower value of k_D than predicted.

Following the treatment of Akcasu, the value of S corresponds to a value of $k_D > 4$ for most of the theories presented. It only agrees with the Altenberger and Deutch[5] hard-sphere result ($S/R_H = 1$) for which $k_D = 2$. Thus the values of S/R_H predicted using R_H/R_G and A_2 are similar, but they disagree with the k_D values found in the DLS experiments.

The results of several theories along with experimental data from this work and others are presented in Figure 3. The earliest theory presented here is from Yamakawa[2,3] and predicts $k_D = 3.2X^3 - 1$. Pyun and Fixman[4] developed an expression of the form $k_D = 8X^3 - 7.16 + \kappa(A)$ where

$$\kappa(A) = 24\int_0^1 \left\{\frac{2\ln[1 + x + (2x + x^2)^{1/2}]}{(2x + x^2)^{1/2}} - 1\right\}x^2 \times \exp[-A(1 - x)^2(2 + x)]\, dx \quad (11)$$

where $x = R/2R_H$ and R is the center of mass separation between polymer pairs. X can be related to A by

$$X = \{3\int_0^1 x^2[1 - \exp[-A(1 - x)^2(2 + x)]]\, dx\}^{1/3} \quad (12)$$

which can be solved numerically for individual values of A. In such a manner $\kappa(A)$ can be determined as a function of X, and thus k_D can be plotted as a function of X. Cotts and Selser[9] described this in more detail. It should be noted, however, that a factor of 2 before the logarithm in eq 22 of their paper (eq 11 above) was omitted.

The treatment by Akcasu and Benmouna[6] gives $k_D = X^2(8X - 6)$. Van den Berg and Jamieson[8] have corrected this result to be frame indifferent with respect to diffusion. This gives $k_D = X^2(8X - 6) - 1$, which is presented in Figure 3. Cotts and Selser have used an approach similar to Akcasu's in combination with their experimental results to predict $k_D = 4.8X^3 - 2$.

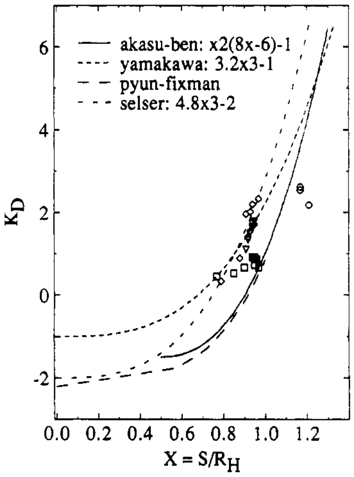

Figure 3. Variation of k_D as a function of $X = S/R_H$. The lines represent various theoretical predictions: (—) Akcasu and Benmouna[6,8] ($k_D = x^2(8x - 6) - 1$); (- - -) Yamakawa[2,3] ($k_D = 3.2x^3 - 1$); (– –) Pyun and Fixman[4] ($k_D = 8x^3 - 7.16 + \kappa(A)$); (- - -) Cotts and Selser[9] ($k_D = 4.8x^3 - 2$). The symbols represent experimental results: (○) polystyrene in 1,1,2,2-tetrachloroethane (from this work); (◇) poly(α-methylstyrene) in toluene;[7,9] (▽) polystyrene in tetrahydrofuran;[10] (□) poly(2-vinylpyridine) in tetrahydrofuran.[11] Further description is provided in the text.

Table 5. Polystyrene, MW 390K, in Toluene—Binary Solution

temp (°C)	viscosity (cP)	diff coeff × 10⁷ (cm²/s)	hydrodyn radius (nm)
20.0	0.708	2.45 ± 0.09	12.37
25.0	0.673	2.65 ± 0.09	12.24
30.0	0.631	2.84 ± 0.10	12.38
45.0	0.537	3.44 ± 0.08	12.61
60.0	0.458	4.29 ± 0.13	12.41
75.0	0.401	5.12 ± 0.24	12.41

The experimental data are provided for good solvents. The Selser and Cotts[7,9] data are for poly(α-methylstyrene) in toluene. The Mandema and Zeldenrust[10] data are for polystyrene in tetrahydrofuran, and that of Chao and Jamieson[11] is for poly(2-vinylpyridine) in tetrahydrofuran. The closest theoretical agreement to the data presented here is the corrected theory of Akcasu and Benmouna.

A summary of some of the above work has appeared in Han and Akcasu[12] and later in Schaefer and Han.[13] Values of k_D and X differed in both the tables and graph for the good solvent data, as compared to those in the original experimental work. There was also a discrepancy in the Pyun–Fixman theoretical result, in particular the plotting of this curve for $X > 1$ where $\kappa(A)$ is no longer defined.

PS in Toluene. The polystyrene fraction was also studied by DLS in toluene. The toluene was spectrophotometric grade supplied by J. T. Baker and used without further purification. The polystyrene concentration was 2.0 mg/mL. Translational diffusion was measured at temperatures between 20 and 75 °C. The viscosity of these samples was also measured. The hydrodynamic radius was seen to be constant with increasing temperature. These values are shown in Table 5. The results show close agreement with literature values reported for similar size polystyrene fractions.[14,32]

DLS Spectra of Polystyrene. The DLS measurements in both solvents were examined in order to determine if processes other than diffusion of the polystyrene coils could be observed. The PS showed a typical linear dependence of the decay constant corresponding to the CONTIN peak Γ vs q^2, indicative of a diffusive process. As previously mentioned, this dependence was used to determine the diffusion coefficient at each temperature. Measurements were made over a range of scattering angles from 20° to 130°. This corresponds to a range in the scattering vector, q, of 6.5×10^{-4} to 1.1×10^{-6} cm^{-1}. The DLS spectra were single exponential within the error of the CONTIN fit. There were indications of a fast relaxation at scattering angles above 90° ($q > 8.5 \times 10^{-5}$ cm^{-1}), but this fast relaxation never had an amplitude above 0.5%. Furthermore, the error in the amplitude of this second relaxation was always greater than 100%. CONTIN analysis with this peak suppressed gave the same result for the translational diffusion coefficient. Analysis with DISCRETE,[33] a program that fits to a discrete sum of exponentials, gave identical results. This indicates that the polystyrene relaxation was a narrow single exponential. The relaxation due to the first internal mode of the polymer coil is predicted to vary in amplitude between 0 and 1% depending on the scattering vector.[34] The relaxation rate is predicted to be very fast, however, and this makes it extremely difficult to reliably observe the internal modes of a polymer coil of this size. Most of the predicted relaxation occurs during the first sample time, which is discarded in our data analysis procedure. The behavior was qualitatively the same at all temperatures.

IV. Conclusion

The PS coil is seen to have a single-exponential DLS spectrum, which arises from the translational diffusion of the coil. The PS coil diffusion coefficients can be described by a virial expansion in concentration up to the linear term in c. The values of k_D, R_H, R_G, and A_2 obtained from DLS and SLS were not consistent with each other according to theoretical predictions, although all of these measured parameters did show that TCE and toluene are good solvents for polystyrene. The change in diffusion coefficient between 1.0 mg/mL and zero concentration was below 10%. Thus the 1.0 mg/mL concentration represents a reasonable approximation to the zero concentration value. The finite concentration values of the PS translational diffusion coefficient, however, are used in the following paper for comparison to the same quantity in ternary solutions, which also contain finite PS concentrations.

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