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## Coil Dimensions of Polystyrenes in Isorefractive Viscous Solvents by Small-Angle Neutron Scattering

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**ABSTRACT:** The radii of gyration of perdeuterated polystyrenes with molecular weights ranging from 10 000 to 104 000 have been determined at infinite dilution in Aroclor 1248 and tricresyl phosphate by small-angle neutron scattering. Measurements were carried out at the National Bureau of Standards, the Oak Ridge National Laboratory, and the University of Missouri. The coherent scattering in all cases is well described by the Debye function. The radii are very close in magnitude to those obtained in cyclohexane at the  $\Theta$  temperature, although for these solvents all indications are that the solvent quality is intermediate to good. This result is interpreted as another manifestation of the solvent dependence of the unperturbed dimensions of polystyrene. Remarkably, however, literature values of the intrinsic viscosity of polystyrenes in these two solvents are considerably higher than those reported in cyclohexane. Thus, in these particular systems the scattering and viscosity experiments are apparently sensitive to quite different properties of the chain, and extraction of coil dimensions directly from intrinsic viscosity data should be performed with caution.

Experiments designed to probe the dynamics of conformational change in solutions of flexible polymers can serve as a valuable tool in molecular characterization, especially in terms of the so-called "internal motions". When combined with information about the radius of gyration, intrinsic viscosity, translational diffusion coefficient, and second virial coefficient, all of which reflect predominantly the behavior of the polymer as a whole, a more complete understanding of macromolecular physics may be developed. The linear viscoelastic (VE) and oscillatory flow birefringence (OFB) techniques in particular have demonstrated the sensitivity and precision necessary to explore the relaxation behavior of isolated polymer chains via extrapolation to infinite dilution.<sup>1-3</sup> The results of both experiments are interpretable in terms of the bead-spring models, and as these models predict, the information content of the two techniques is essentially identical, at least at low and intermediate frequencies.<sup>4</sup> However, OFB

has been shown to exhibit greater sensitivity and precision when infinite dilution properties are of interest.<sup>3</sup> For polymers dissolved in "typical" solvents with viscosities around 1 cP (e.g., toluene, benzene, and THF), the time scales relevant to conformational rearrangement range from nanoseconds to milliseconds, whereas OFB and VE apparatuses generally operate up to at most a few kilohertz. Thus, internal modes would be largely inaccessible via these techniques. This difficulty may be overcome by the use of viscous solvents and the principle of time-temperature superposition; for example, in the polystyrene/Aroclor system, infinite dilution OFB results have been reported up to reduced frequencies corresponding to a time scale of tens of nanoseconds in a low-viscosity solvent.<sup>3</sup> Unfortunately, as well-suited as solvents such as Aroclors and tricresyl phosphate (TCP) are to conformational dynamics experiments, they are essentially isorefractive with polystyrene. As a consequence, it is very difficult to obtain radius of gyration, translational diffusion, and second virial coefficient information by established light scattering methods. Therefore, although the bead-spring model is

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Table I

	NBS	ORNL	MURR
wavelength, Å	6.0 ± 1.5	4.75 ± 0.28	4.75 ± 0.19
source iris diameter, cm	2.7	3.5	2.5
sample iris diameter, cm	1.2	1.2	1.0
source-to-sample distance, m	4.5	3.5	4.5
sample-to-detector distance, m	3.60	4.51	4.59
beam stop diameter, cm	5.7	8	4

very successful in describing infinite dilution VE and OFB properties in these systems, the significance of the parameter values thus obtained is not clear. For example, it would be most illuminating to ascertain whether a given set of values for the number of subchains  $N$ , the subchain friction factor  $\zeta$ , and the hydrodynamic interaction parameter  $h^*$  can adequately describe VE, OFB, intrinsic viscosity, coil radius, and translational diffusion data. The recent development and application of techniques such as small-angle neutron scattering (SANS) and forced Rayleigh scattering to polymer problems offers an opportunity to circumvent this difficulty and thus to obtain a more complete body of data on one or more polymer-solvent systems. Toward this end, in this paper we report the radii of gyration of perdeuterated polystyrene fractions, extrapolated to infinite dilution, measured by SANS. Radii have been obtained for five molecular weights in TCP and for four samples in Aroclor 1248, covering the molecular weight range  $1 \times 10^4$  to  $1 \times 10^5$ .

## Experimental Section

**Materials.** Perdeuterated polystyrenes (dPS) were obtained from Polymer Laboratories, Ltd. The manufacturer's molecular weight specifications are as follows:  $M_w = 10\,000$ ,  $M_w/M_n = 1.06$ ;  $M_w = 24\,600$ ,  $M_w/M_n = 1.06$ ;  $M_w = 45\,000$ ,  $M_w/M_n = 1.05$ ;  $M_w = 64\,300$ ,  $M_w/M_n = 1.07$ ;  $M_w = 104\,000$ ,  $M_w/M_n = 1.07$ ;  $M_w = 215\,000$ ,  $M_w/M_n = 1.12$ . All these  $M_w$  values have been scaled by the monomer molecular weight ratio to correspond to hydrogenated polystyrene. Tri-*m*-tolyl phosphate (TCP) was obtained from the Eastman Kodak Co. and pretreated to remove trace volatile impurities.<sup>5</sup> Aroclor 1248, lot no. KM 502 (A1248), is a product of the Monsanto Chemical Co. and was generously donated by Dr. J. L. Schrag of the University of Wisconsin; it was used without further treatment. Solutions were prepared gravimetrically, with dissolution assisted by gentle heating (<50 °C); each solution was allowed to come to equilibrium for at least 1 month prior to use. Weight concentrations were converted to g/cm<sup>3</sup> by assuming additivity of volumes and densities of 1.14, 1.16, and 1.45 cm<sup>3</sup>/g for dPS, TCP, and A1248, respectively.

**Measurements.** SANS measurements were performed at the National Bureau of Standards (NBS), at the Oak Ridge National Laboratory (ORNL), and at the University of Missouri (MURR), involving a total of five sessions of from 3- to 5-day duration, spread over 3 years. The salient features of the three spectrometers have been described in the literature;<sup>6-8</sup> the geometries employed for this work are listed in Table I. All solutions were contained in unsealed 2-mm path length quartz cells; both TCP and A1248 display negligible evaporation at room temperature. No special attempt was made to control the temperature of the solutions; the ambient temperature ranged from 21 to 25 °C.

For these samples, which are of necessity dilute in the scattering polymer, run times varied from 4 to 16 h. Unfortunately, the hydrogen content of TCP leads to a substantial incoherent background, and in A1248 the chlorines absorb significantly in addition to the hydrogen incoherent signal. As a consequence, the transmission factors were between 0.45 and 0.55 for all solutions, and longer cells could not be employed to increase the signal-to-noise ratio. The data reduction was essentially the same in all cases. The two-dimensional detector count arrays were normalized to the incident neutron flux by presample monitor counts. Background counts, obtained by using cadmium to block the incident beam, were subtracted from all runs. Scattering from an empty cell, weighted by the appropriate relative transmission

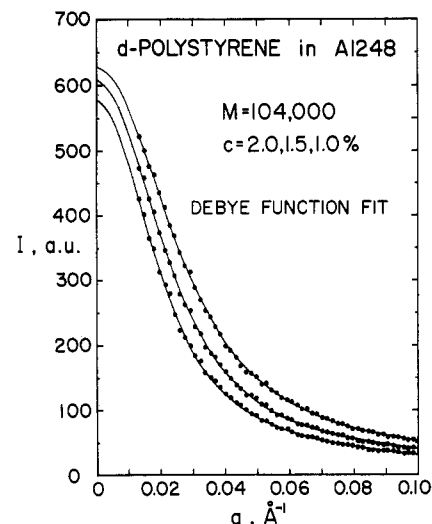


Figure 1. Coherent scattering from three solutions of d-polystyrene in Aroclor 1248 and the best-fit Debye function as determined by nonlinear regression.

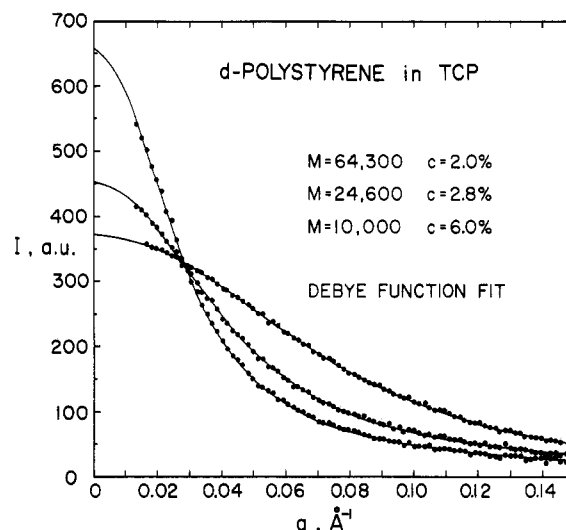


Figure 2. Coherent scattering from three solutions of d-polystyrene in tricresyl phosphate and the best-fit Debye function as determined by nonlinear regression.

factor, was subtracted from each set of solution or pure solvent data. The solvent contribution, weighted by its volume fraction, was then subtracted from each solution data set in a separate step. The spatial sensitivity of each detector was assessed by using pure water samples. Only at ORNL was it necessary to correct the data for significant sensitivity variation. This was accomplished by means of standard software procedures which also performed the cell-by-cell corrections for backgrounds for both sample and solvent runs. The corrected data, still in array form, were then radially averaged to generate the  $I(q)$  vs.  $q$  format appropriate for analysis;  $q$  is the scattered wave vector given by  $q = (4\pi/\lambda) \sin(\theta/2)$ , where  $\lambda$  is the neutron wavelength and  $\theta$  the scattering angle.

One intrinsic viscosity measurement was made with a capillary viscometer. The temperature was maintained at  $25.06 \pm 0.02$  °C during the measurements, with the temperature established by means of thermistors calibrated to within  $\pm 0.005$  °C against a platinum resistance thermometer with a calibration traceable to NBS.

## Results

Typical  $I(q)$  vs.  $q$  curves are presented in Figures 1 and 2. In the former, the coherent scattering from three different dilute solutions of the 104 000 mol wt sample in A1248 is displayed, showing the effect of increasing con-

centration: enhancing the scattered intensity but decreasing the apparent radius of gyration  $R_g$ , as expected. The absolute value of the scattered intensity has no significance in these plots, but for a given sample/solvent pair the relative values at different concentrations should reflect the relative cross sections. In Figure 2 scattering curves for three different molecular weights in TCP are plotted, for selected concentrations; the evolution of the shape of the scattering function with increasing molecular weight is clearly revealed. These data were all acquired at NBS, and the amount of scatter evident in the data is representative of all the NBS measurements. The scattering curves acquired at ORNL and MURR display visibly more scatter, but not enough to affect the subsequent analysis. These differences are ascribable primarily to variations in flux, detector resolution, and detector homogeneity.

For all solutions apparent radii of gyration were obtained by fitting the scattering curve to the Debye function by nonlinear regression

$$I(q) = [2A/(qR_g)^4] \{e^{-q^2 R_g^2} - 1 + q^2 R_g^2\} + B \quad (1)$$

with  $A$ ,  $B$ , and  $R_g$  as free parameters. Ideally, it would be preferable to use the Zimm plot approach to extract  $R_g$ , to avoid making a priori assumptions about the monomer distribution function. This is not possible with these data, however, for two reasons. For all but the lowest molecular weights, the  $q$  range does not extend sufficiently into the Guinier regime to avoid curvature in an  $I^{-1}(q)$  vs.  $q$  plot; furthermore, the inevitable uncertainty in the subtraction of the incoherent background has a substantial effect on the values of  $I^{-1}(q)$ . The data in Figures 1 and 2 indicate that the Debye function describes the observed scattering extremely well; furthermore, this approach has the advantage of utilizing data obtained over the entire accessible  $q$  range in the extraction of  $R_g$ . In the fitting procedure the base line was left as an adjustable parameter, even though the solvent scattering had been subtracted. Resulting residual incoherent levels were typically 1–10% of  $I(0)$  and occasionally negative. This may be attributed to uncertainty in the subtraction procedure due to low signal-to-noise ratios, finite  $q$  ranges, small differences between different solution cells, and the appropriateness of the use of the solvent volume fraction as the relevant weighting factor. However, for some of the solutions where the residual incoherent signal was particularly large, the data were fit with the Debye function prior to subtraction of the solvent scattering.  $R_g$  values thus obtained were within one- or two-tenths of an angstrom of those extracted in the manner described above. Thus, any uncertainty in the solvent scattering subtraction does not markedly influence the final results.

The Debye function was derived for a Gaussian equilibrium distribution of scattering centers, and thus its application to a non  $\Theta$  polymer/solvent system might appear inappropriate. However, there is considerable justification, both theoretical and experimental, for this approach. For example, it has been shown that the scattering function for an excluded volume chain and the Debye function are of essentially identical shape, particularly in the relevant  $qR_g$  range, and that  $R_g$  for a swollen coil can be obtained directly.<sup>9,10</sup> SANS measurements on dPS in toluene<sup>11</sup> and CS<sub>2</sub>,<sup>12</sup> both good solvents, have been well described by the Debye function; the same data were not describable by an excluded volume model such as that due to Ptitsyn.<sup>13</sup> Similarly, light scattering measurements on high molecular weight polystyrenes in benzene were also in close agreement with the Debye function.<sup>14</sup> On the basis of these results, and the success of the Debye function fit

Table II  
Solution Concentrations Used

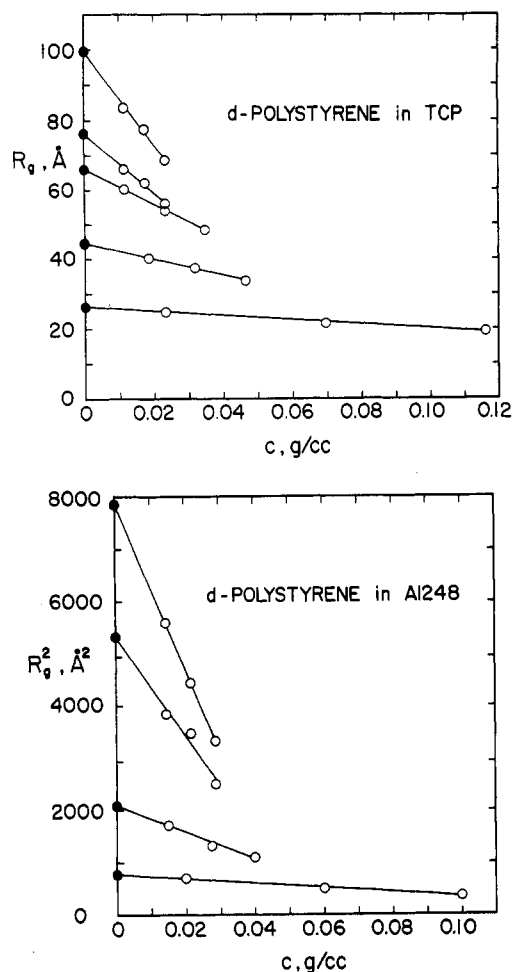
$M_w$	TCP <sup>a</sup>	A1248 <sup>a</sup>
10 000	0.0232	0.0201
	0.0695	0.0601
	0.116	0.0999
24 600	0.0185	0.0150
	0.0319	0.0275
	0.0464	0.0399
45 000	0.0116	
	0.0232	
	0.0348	
64 300	0.0115	0.0145
	0.0174	0.0217
	0.0232	0.0288
104 000	0.0116	0.0144
	0.0174	0.0217
	0.0232	0.0288

<sup>a</sup> In g/cm<sup>3</sup>.

as evidenced in Figures 1 and 2, there is strong reason for confidence in the  $R_g$  values thus obtained.

One important consideration with this fitting procedure is determining the smallest  $q$  datum to be included in the fit. (In principle, for a given spectrometer and scattering geometry, the usable  $q$  range is known from experience and/or the results from scattering standards. However, for these solutions, where the signal-to-noise ratio is so low, the usable  $q$  range was always contracted at the low- $q$  end at all three facilities.) For the higher molecular weight samples in particular, the smaller  $q$  data fall in the steepest portion of the curve, and it is possible that the value of  $R_g$  extracted would show considerable sensitivity to the last point included. In fact, this was not the case. For all samples, the four  $I(q)$  points corresponding to the four lowest  $q$  values were successively removed from the fit and the resulting  $R_g$  values compared. In no case did the  $R_g$  values vary by more than 1 or 2 Å, and the variation was usually less than that. Furthermore, the variation in  $R_g$  showed no systematic trend as the  $q$  range was reduced, and the quality of the fit (as assessed via the usual  $\chi^2$  parameter) was unchanged. As an example, for the highest molecular weight sample in A1248, where the problem should be most acute, the four  $R_g$  values obtained were 75.5, 75.3, 74.0, and 74.3 Å for the lowest concentration; 66.6, 67.1, 66.4, and 66.3 Å for the intermediate concentration; and 57.6, 57.6, 57.7, and 58.0 Å for the highest concentration. Final  $R_g$  values were determined by averaging each set of four results.

For each sample/solvent pair, measurements were made at three concentrations in the dilute regime. The concentrations used are listed in Table II. The  $R_g$  value determined for each concentration was then used to obtain an infinite dilution radius by extrapolation. Two extrapolation methods were used: one a direct extrapolation of  $R_g(c)$  vs.  $c$ , the other of  $R_g^2(c)$  vs.  $c$ . The latter has some theoretical justification,<sup>15</sup> but for practical purposes the difference between the two extrapolations hinges on the relative weighting of the  $R_g(c)$  values. The first method is demonstrated for the TCP data in Figure 3a, while the second is illustrated for the A1248 data in Figure 3b. Within the uncertainty of each individual  $R_g(c)$  value, both extrapolation methods are linear and provide similar intercept values. The largest difference found was for the 104 000 dPS in A1248, with the  $R_g(0)$  value for the  $R_g^2(c)$  extrapolation being 3.4 Å less. In the remaining discussion, all  $R_g(0)$  values represent the average of the two intercepts. In Table III the infinite dilution radii of gyration are listed, along with the spectrometer and  $q$  range employed and the date of the measurements.



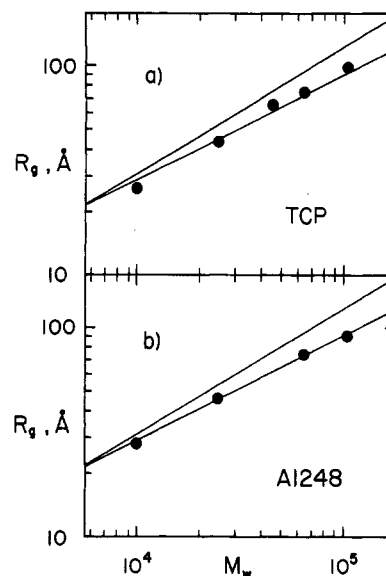
**Figure 3.** Extrapolation of the radius of gyration to infinite dilution for various molecular weights of d-polystyrene: (a) in trisresyl phosphate, plotted as  $R_g$  vs. concentration; (b) in Aroclor 1248, plotted as  $R_g^2$  vs. concentration.

**Table III**

$M_w$	solvent	location	date	$q$ range, $\text{\AA}^{-1}$	$R_g$ , $\text{\AA}$
10 000	TCP	NBS	2/83	0.013–0.15	26.1
	A1248	ORNL	6/85	0.016–0.14	28.0
24 600	TCP	NBS	2/83	0.013–0.15	44.1
	A1248	ORNL	6/85	0.016–0.14	45.9
45 000	TCP	NBS	5/82	0.015–0.12	65.5
64 300	TCP	NBS	2/83	0.013–0.15	75.5
	A1248	NBS	3/85	0.013–0.10	74.0
104 000	TCP	MURR	12/84	0.009–0.09	98.1
	A1248	NBS	3/85	0.013–0.10	90.3

The infinite dilution radii are plotted as  $\log R_g$  vs.  $\log M_w$  in parts a and b of Figure 4 for TCP and A1248, respectively. Included on these plots are lines representing polystyrene radii in  $\theta$  and good solvents, measured by SANS and light scattering, as a reference.<sup>16,17</sup> It is clear that in both solvents deuterated polystyrenes in this molecular weight range have dimensions very close to those of polystyrene in cyclohexane at the  $\theta$  temperature. This result is somewhat unexpected, as intrinsic viscosity measurements on both TCP and A1248 solutions of polystyrene indicate a solvent quality that is at least "moderately good".<sup>5,18</sup> The 45 000 dPS in TCP radius appears to be somewhat high relative to all the others; the reason for this is not clear.

If the data are fitted to a straight line, molecular weight exponents of  $0.57 \pm 0.01$  and  $0.50 \pm 0.01$  are obtained for TCP and A1248, respectively; the TCP value does not change appreciably if the 45 000 datum is ignored. The implication of these values is that TCP is indeed a mod-



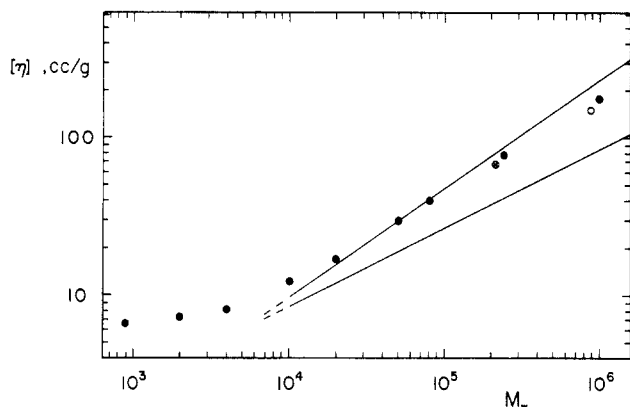
**Figure 4.** Radius of gyration at infinite dilution vs. molecular weight for d-polystyrene (a) in trisresyl phosphate and (b) in Aroclor 1248. The straight lines correspond to radii for d- and h-polystyrene in good solvents (upper line) and  $\theta$  solvents (lower line), as determined by SANS and light scattering.

erately good solvent, while A1248 is very close to a  $\theta$  solvent. Thus the TCP exponent contrasts with the magnitude of the radii, while the A1248 exponent conflicts with the intrinsic viscosity results. However, these exponents should be viewed with a great deal of caution. In the first instance, the range of molecular weights used is not as great as is desirable to establish a power law exponent. Small changes in  $R_g$  values can lead to significant variation in the resulting exponent. In particular, the difference between the exponents in TCP and A1248 derives primarily from the 104 000 data alone. Furthermore, there is some indication that this A1248 value may be 2–3  $\text{\AA}$  low.<sup>35</sup> The more crucial point, however, is that if indeed these solvents are of intermediate or "marginal" quality, a unique exponent will not be obtained. Rather, at the lower molecular weights  $\theta$ -like behavior should be observed, with a crossover to excluded volume behavior at some higher molecular weight range. Radii for significantly higher molecular weights would be necessary to evaluate this possibility; unfortunately, the combination of low signal-to-noise ratio for these systems coupled with instrumental restrictions on the available  $q$  range makes completion of such measurements problematic.

## Discussion

The SANS results reported here raise questions about the behavior of polystyrene in these viscous solvents, of which the most salient is why the radii are close to  $\theta$  solution values when the intrinsic viscosities are so much larger than their  $\theta$  solvent counterparts. In Figure 5 values of  $[\eta]$  for h-polystyrene in A1248 are reproduced from ref 18, and also one value in TCP.<sup>5</sup> As a comparison, literature data for polystyrene in toluene, a good solvent, and in  $\theta$  solvents are represented by straight lines.<sup>19,20</sup> These results illustrate why the two viscous solvents are considered as at least moderately good and of essentially equivalent quality. Before discussing any implications of these results, it is important to assess the possible role of systematic errors in the measurements.

The SANS results could be reconciled with the  $[\eta]$  values directly if the  $R_g$  values were systematically low. However, it is not easy to identify such a systematic error. Although SANS from polymers in general, and from these solutions



**Figure 5.** Intrinsic viscosity of polystyrene in various solvents: (upper line) h-polystyrene in toluene;<sup>19</sup> (lower line) h-polystyrene in cyclohexane;<sup>20</sup> (●) h-polystyrene in Aroclor 1248;<sup>18</sup> (○) h-polystyrene in tricresyl phosphate;<sup>5</sup> (⊗) d-polystyrene in Aroclor 1248.

in particular, is often plagued by low signal-to-noise ratios, it is not clear how this would result in systematically low radii being extracted. Certainly, the problems associated with dust, stray radiation, source fluctuations, etc., which are endemic to light scattering, are easily dealt with in SANS. The use of the Debye function is justified on both theoretical and experimental grounds, as discussed previously. Nor may it be argued that its use inherently leads to low  $R_g$  values because a value of approximately 125 Å for the 104 000 sample in toluene was obtained in just this manner.<sup>11</sup> The insensitivity of the  $R_g$  value to the lowest  $q$  datum included, coupled with the excellent fit over the entire  $q$  range, suggests that any systematic error present cannot affect the shape of the scattering curve substantially, nor may it be concentrated in a small range of  $q$ . The difficulty in obtaining an exact subtraction of the solvent contribution has been demonstrated to have no effect on the results. The wavelength distribution of the incident beam, especially at NBS, could be considered as a source of error. However, using a weighted average of  $\lambda$  results in at most a 1% change in the  $R_g$  values obtained, and in the opposite direction (i.e., the value of  $R_g$  obtained would decrease).<sup>12,21</sup> In sum, when the SANS data are viewed as a whole and it is borne in mind that they were acquired on three quite different spectrometers and over 3 years on the NBS spectrometer (which underwent considerable hardware and software modification over that period), it is difficult to picture a systematic error which is not inherent in the SANS process itself. Yet SANS has been shown to yield radii identical with those obtained via light scattering.<sup>17</sup> One last possibility is that the deuteration of the polymer has a profound influence on the radii. This must be considered as highly unlikely, however. In the polystyrene/cyclohexane system, deuteration of one of the components results in a shift in the  $\Theta$  temperature of approximately 5 °C.<sup>22</sup> The resulting change in  $R_g$  would be difficult to detect for the systems considered here.<sup>23</sup> As an additional check, the intrinsic viscosity of the 215 000 sample of d-polystyrene has been measured in A1248 at 25.06 °C. The result is shown in Figure 5, from which it can be seen that deuteration has no significant effect on the long-range hydrodynamics.

Possible systematic errors in the measurement of  $[\eta]$  should also be considered, but are at least as difficult to imagine. The h-polystyrene/A1248 results reported were obtained in a Couette viscometer, where the shear rate is easily controlled. These results are also in complete agreement with other  $[\eta]$  measurements for h-polystyrene in Aroclor solvents.<sup>24</sup> The d-polystyrene result reported

here was obtained in a Cannon-Ubbelohde viscometer but at extremely low flow rates, so no kinetic energy corrections were required.

On the basis of the results presented here, combined with the extensive literature on the dynamics of polystyrene in Aroclor solvents, there is no reason to reassess the consideration of these solvents as being of intermediate quality. As discussed previously, a great deal of significance should not be attached to the values of the molecular weight exponents. In particular, although the A1248 results yield an exponent of  $0.50 \pm 0.01$ , this is definitely not a  $\Theta$  system. In addition to the intrinsic viscosity results reproduced in Figure 5, this conclusion is supported by the positive second virial coefficient indicated by the slopes of the extrapolations in Figure 3b and by the fact that a solution of polystyrene of very high molecular weight ( $44 \times 10^6$ ) in A1248 did not precipitate at temperatures as low as  $-1.4$  °C.<sup>25</sup> Rather, these results support the concept of a crossover from Gaussian statistics at low molecular weight to excluded volume statistics at higher molecular weight for solvents of intermediate quality. This interpretation also suggests that TCP is of somewhat higher quality than A1248. However, this is not supported by the single intrinsic viscosity measurement for polystyrene in TCP, but as will be discussed below, it is not clear how direct a correlation exists between coil size and intrinsic viscosity for these systems.

The notion of the crossover from Gaussian to excluded volume statistics has been put on a quantitative basis via the blob model<sup>26</sup> and modifications thereon. For example, this approach can be used to estimate the expansion factors corresponding to the radii reported here. When the compilation of Han for intrinsic viscosities of polystyrene in various solvents<sup>20</sup> and the intrinsic viscosity of the highest molecular weight in A1248 reported<sup>27</sup> are taken, a value of the reduced molecular weight  $N/N_c$  of 75 is obtained. Here,  $N$  is the number of subunits in the chain, while  $N_c$  is the temperature-dependent cutoff between Gaussian and excluded volume regimes;  $N_c$  becomes infinite in a  $\Theta$  solvent. The highest molecular weight value was used in order to be as far into the asymptotic region as possible. When the good solvent limiting exponent for  $R_g$  is taken to be 0.6, expansion factors of 1.08, 1.03, and 1.00 are obtained for the 104 000, 64 300, and 24 600 samples in A1248, respectively, by using the expression of Farnoux et al.<sup>26</sup> This analysis should only be viewed as providing a rough estimate of the unperturbed dimensions. One difficulty is that the implicit assumption is made that the intrinsic viscosity and SANS measurements reflect the same properties of the chain, whereas these results may suggest otherwise. Furthermore, the dynamic property,  $[\eta]$ , is closer to good solvent behavior than the static property,  $R_g$ , is a given temperature and molecular weight. This is in contrast to the known behavior of the hydrodynamic radius,  $R_h$ , relative to  $R_g$ .<sup>20</sup>

It has been well established that the unperturbed dimensions of polymers in general, and certainly polystyrene, are solvent-dependent. The principle mechanism is presumed to be local polymer-solvent interactions, which alter the probability distribution of internal chain bond angles. For pure solvents (as opposed to mixed systems) it has been proposed that polystyrene can adopt conformations in acyclic solvents which lead to smaller dimensions than in cyclic solvents.<sup>28</sup> However, as has been pointed out, the polarity of the solvent could be at least as important, and solvent interaction with the phenyl side group may be the crucial factor.<sup>29,30</sup> In nonpolar solvents such as cyclohexane the unperturbed dimensions (via intrinsic viscosity) are

up to 15% greater than in other solvents such as diethyl malonate ( $\Theta$  temperature 36 °C).<sup>29,30</sup> Therefore, these results for polystyrene radii in Aroclor via SANS are quite consistent with those in other solvents by intrinsic viscosity and light scattering. In addition, the strong temperature dependence of viscosity for Aroclor solvents suggests the possibility of solvent structure; it is quite conceivable that the polymer dimensions would be affected.

Certain features of the results reported here are similar to observations recently reported by Huber et al.<sup>23</sup> Included in their results are some light scattering and SANS measurements of low molecular weight polystyrenes in toluene and cyclohexane. Of particular interest is the appearance of a molecular weight exponent "significantly lower than 0.595" in toluene for a small molecular weight range below 100 000. Moreover, at still lower molecular weights the exponent increases again. The results in Figure 4, if examined closely, may indicate a similar trend, particularly for  $M < 50\,000$ .

The preceding discussion has focused on possible interpretations of the coil radii results without factoring in the intrinsic viscosity behavior in Aroclor 1248 at low molecular weight. The results in Figure 5 indicate the presence of an additional contribution to the intrinsic viscosity by the leveling off as  $M$  decreases and by the fact that the absolute magnitude exceeds that in toluene in this regime. This viscosity enhancement is quite possibly intimately connected to the observation of additional contributions to the viscoelastic and oscillatory flow birefringence properties at high frequencies, as has been discussed.<sup>31-34</sup> It is still not clear, however, what the exact origin(s) of this behavior is (are) nor how the measured dynamics properties should be interpreted to extract the pure polymer chain contribution. Thus, at this stage it is not possible to say how much intrinsic viscosities in these solvents reflect the coil dimensions directly. It is important to emphasize that of all the techniques available to determine coil dimensions, either direct or indirect, SANS is in a sense the least susceptible to the influence of specific polymer/solvent interactions. The reason for this is that SANS reflects spatial correlations purely between nuclei and is essentially independent of chemical bonding, hydrodynamic interaction, internal electric fields, solvent orientation, etc., which may contribute to measured light scattering or viscosities.

## Conclusions

The results presented indicate that coil dimensions of polystyrenes in dilute Aroclor and TCP solutions are accessible by SANS, at least for molecular weights up to 100 000. In this molecular weight range the coherent scattering is described extremely well by the Debye function. The radii of gyration at infinite dilution have values very close to those obtained by other workers in cyclohexane; however, the solvent quality is intermediate to good. There is some indication in the results that TCP may be a slightly better solvent than A1248. Estimates of the unperturbed dimensions in A1248, obtained via the blob hypothesis, suggest that they are approximately 5–10% less than in cyclohexane for a molecular weight of 104 000. This is quite reasonable in light of the known dependence of the unperturbed dimensions of polystyrene on solvent structure and/or polarity. The coil radii are surprising in view of the intrinsic viscosity results for the same systems, which are considerably larger than in cyclohexane. However, the additional contribution to the intrinsic viscosity, clearly evident at low molecular weight, raises questions about the direct extraction of coil dimensions from viscosity measurements in these solvents.

It is quite possible that SANS and intrinsic viscosity are sensitive to somewhat different properties of these solutions.

In the future it will be appropriate to determine the radius of gyration as a function of temperature, both as an additional assessment of the solvent quality and as a test of the assumption, implicit in the use of time-temperature superposition in conformational dynamics experiments, that the solvent is effectively athermal over the relevant temperature range. Measurements at higher molecular weight would be very useful, but preliminary results on a sample with molecular weight 215 000 suggest that the molecular weight range may not be extended significantly with currently available SANS instrumentation.<sup>35</sup> The difficulty arises from the low signal-to-noise ratio inherent in these systems due to modest contrast factors, low polymer concentrations, and substantial incoherent scattering.

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**Registry No.** PS, 9003-53-6; TCP, 563-04-2; Aroclor 1248, 12672-29-6; neutron, 12586-31-1.

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## Dynamics of Semidilute Solutions Using Photon Correlation Spectroscopy: The Influence of Solvent Quality

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**ABSTRACT:** Photon correlation spectroscopy data are presented for a high molecular weight ( $3 \times 10^6$ ) polystyrene fraction in the ethanol/ethyl acetate (isorefractive) mixed-solvent system at semidilute concentrations. Solvent quality decreases with increasing ethanol, and  $\Theta$ -conditions are approached at 10% ethanol. Two characteristic components may be resolved from the time correlation function using multiexponential analysis over the whole range of solvent quality: (a) a fast (gel) mode, with a concentration exponent decreasing progressively to zero under  $\Theta$ -conditions; (b) a slow (hydrodynamic) mode with a concentration dependence becoming strongly negative at  $\Theta$ -conditions. These results harmonize with previous measurements in the  $\Theta$ -system PS/cyclopentane at 21 °C. While the contributions of several modes in semidilute solutions have been described previously, the progressive change in the exponent  $D \sim C^\gamma$  as a function of solvent quality has not earlier been documented.

Previous communications<sup>1-3</sup> reported the use of a bimodal model to interpret the diffusive behavior of high molecular weight polystyrenes in semidilute solution, both in a thermodynamically good solvent (THF) and a  $\Theta$ -solvent (cyclopentane, 21 °C), as well as in the marginal solvent ethyl acetate.<sup>4</sup> Measurements were made with photon correlation spectroscopy (PCS) in the range of  $q$  vector corresponding to  $qR_g > 1$  but restricted to the  $q$  range in which  $(\Gamma_q/q^2)$  was strictly  $q$  independent at each concentration. (Here  $\Gamma_q$  is the measured relaxation rate at finite values of  $q$ , the scattering vector, and  $R_g$  is the radius of gyration of an isolated coil.) For further details, the relevant papers, ref 1-4, should be consulted.

Use of the cumulants method<sup>5</sup> to interpret the time correlation function showed that the normalized second cumulant,  $\mu_2/\bar{\Gamma}^2$ , was large in the various systems and changed systematically with concentration. Some typical data are shown in Figure 1 for the fraction with  $M_w = 8 \times 10^6$ . This observation suggests the possible presence of several relaxational modes, a feature that was examined in some detail by Chu and Nose for the polystyrene/*trans*-decalin system.<sup>6</sup> When such semidilute solutions are diluted to the dilute regime and reexamined at low angles, they are characterized by essentially single-exponential correlation functions, which effectively refutes polydispersity as a source of the large second cumulant. In order to explore possible sources of this behavior, multiexponential analysis of the time correlation function was used. Using the usual statistical parameters for judging "goodness of fit",<sup>1</sup> this approach gave two molar-mass-independent components in each of the three solvents but with different relative weighting. (This fit was selected as the simplest consistent with the data,<sup>1</sup> but we cannot exclude more complicated alternatives.) These data are summarized in Figure 2 as log-log plots of the dynamic correlation length,  $\xi_D$ , vs. concentration. The correlation length is a convenient way of unifying the presentation of

data in different media where the focus is on the relative concentration dependences.  $\xi_D$  is defined for each mode as

$$\xi_D = kT/6\pi\eta_0 D \quad (1)$$

where  $k$  is Boltzmann's constant,  $T$  the absolute temperature,  $\eta_0$  the solvent viscosity, and  $D = (\Gamma_{\text{fast}}/q^2)$  or  $(\Gamma_{\text{slow}}/q^2)$ . The relaxation rate for each component was estimated by using eq 2, and the respective  $D$  values were obtained as the slopes of linear plots of  $\Gamma_{\text{fast}}$  and  $\Gamma_{\text{slow}}$  vs.  $q^2$ . Figure 3 depicts the data obtained in the  $q$  range corresponding to  $qR_g < 1$ .

Comparison of the data showed the following:

1. The data for the fast component at  $qR_g > 1$  fall on the same curve as those for the fast component at  $qR_g < 1$ . Thus, a single  $q^2$ -dependent and molar-mass-independent relaxation is probed over the  $q$  range where  $q\xi < 1$  (i.e., the hydrodynamic regime) and the solution behaves as a transient gel formed by chain entanglements as anticipated from the theory of de Gennes.<sup>7</sup>

2. The values of  $(\Gamma_q/q^2)$  for the slower molar-mass-independent mode at  $qR_g > 1$  (also  $q$  independent) were found to lie on an extension of the curve for the data obtained in dilute solution at low angles (single exponentials and corresponding to translational diffusion of the isolated coil). At  $qR_g < 1$ , however, using a correspondingly greater probing length, the slower mode is molar mass dependent (Figure 3) in the poorer solvents ethyl acetate and cyclopentane. (In the good solvent only the gel mode is detected at  $qR_g < 1$ .)

3. The exponent characterizing the concentration dependence of the dynamic length ( $\xi_D \sim C^\gamma$ ) was found to range for the fast component from 0.57 in THF to about zero in the  $\Theta$ -system. With the slower mode,  $\gamma$  decreases from 0.44 (THF) to a negative value (-0.45) in the  $\Theta$ -solvent. The corresponding exponents in ethyl acetate<sup>4</sup> were intermediate between those in THF and cyclopentane, 0.33