Effects of Deuteration of a Polystyrene Chain on Its Thermodynamics and Hydrodynamics in Cyclohexane around the Flory Θ-Temperature: The Static and Dynamic Laser Light Scattering Investigation

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Received July 22, 1997; Revised Manuscript Received September 8, 1997 [⊗]

ABSTRACT: The average radii of gyration $\langle R_g \rangle$ and hydrodynamic radii $\langle R_h \rangle$ of a set of deuterated polystyrene (DPS) standards with different molar masses in cyclohexane around its Θ-temperature were precisely measured by using static and dynamic laser light scattering. On the basis of these values, the mean segment size (l = 0.331 nm) and chemistry-dependent constant (ν_T = 1.10) used in the renormalization group theory were calculated. In comparison with a normal polystyrene (PS), DPS has a smaller l and a larger ν_T. The smaller l indicates that at the Θ-temperature a DPS chain has a smaller conformation (i.e., coils more) than a PS chain with the same contour length. The larger ν_T indicates that in a good solvent a DPS chain extends more than a PS chain for a given increase of the reduced temperature $(T - \Theta)/\Theta$. Our results showed that the difference in thermodynamics also leads to an opposite and different temperature dependence of the hydrodynamic radius $\langle R_h \rangle$ for DPS and PS in cyclohexane.

Introduction

Due to the large difference among the neutron-scattering lengths of protons or deuterons and the rest of the atoms in a polymer chain, the deuteration of a polymer has become a standard labeling method in neutron scattering for monitoring a single polymer chain in the presence of many other polymer chains. It provides a basis for the studies of chain dimensions, local chain dynamics, and thermodynamic interactions in melts, dense systems, and concentrated solutions.[1−4] In addition to its use in neutron scattering, the deuteration of a polymer chain is also used in nuclear magnetic resonance (NMR). It has always been assumed that the deuteration has no effect on the thermodynamics and conformation of a polymer chain, so that a deuterated chain is a true representative of all the polymer chains in the system.

However, this assumption has recently been challenged by a number of reports related to the effect of deuteration on thermodynamics of polymer blends[5−7] and polymer solutions.[8,9] Unfortunately, these effects, if they exist, were generally ignored in most data analysis. The effects of deuteration are mostly observable when the system is near its critical points, e.g., the Flory Θ-temperature, at which the overall interactions are delicately concealed and even a small additional contribution can significantly shift the critical points. For example, normal polystyrene (PS) and deuterated polystyrene (DPS) have different Θ-temperatures and solubility parameters in cyclohexane.[8] It has also been shown that PS and DPS have a similar mean segment size l, but different chemistry-dependent constants ν_T which is only affected by thermodynamic interactions.[9]

To our knowledge, the accurate and consistent experimental data of deuterated polymers are still missing, which prevents a reliable determination of the mean segment size l_D and chemistry-dependent constant $\nu_{T,D,}$ where the subscript D represents the deuterated polymer. On the other hand, the deuteration of a polymer chain might also effect its hydrodynamics if it effects its thermodynamics. The main objective of this study is to measure the accurate values of the average radius of gyration $\langle R_g \rangle$ and hydrodynamic radius $\langle R_h \rangle$ of a set of narrowly distributional DPS standards around its Θ-temperatures by using a combination of static and dynamic laser light scattering (LLS), so that we will be able to calculate l and ν_T used in the renormalization group theory and evaluate the reported difference between PS and DPS.

Theoretical Background

Using the renormalization group theory, Schäfer[10] calculated the experimentally accessible correlation lengths and thermodynamic quantities of a dilute polymer solution. The theory is based on a model of self-repelling Gaussian chains characterized in terms of the mean segment size (l), the number of segments per chain (N), and the excluded volume constant (β). According to its definition, the excluded volume vanishes at the Θ-temperature. In order to prevent the breaking down of the expansion parameter ($\beta N^{1/2}$) for a long polymer chain ($N \gg 1$) at $T > \Theta$, the renomalization has been used to generate the starting values in terms of the parameters:

$$R_\Theta^{\ 2} = l^{\,2} N \qquad (1)$$

$$Z = \beta N^{1/2} = \nu_T N^{1/2}(T - \Theta)/\Theta \qquad (2)$$

where R_Θ is the radius of a polymer chain at its

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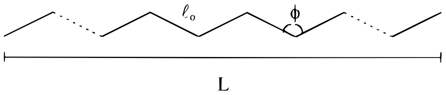
[⊗] Abstract published in *Advance ACS Abstracts,* October 15, 1997.

S0024-9297(97)01104-2 CCC: $14.00

Table 1. Weight-Average Molar Mass (M_w) and Polydispersity Index (M_w/M_n) of Five Dueterated Polystyrene (DPS) Samples and a Normal Polystyrene (PS) Sample

sample	DPS-1	DPS-2	DPS-3	DPS-4	DPS-5	PS-5
$M_w/10^3$ (g/mol)	117	198	354	471	990	1050
M_w/M_n	1.06	1.06	1.12	1.08	1.09	1.08

Θ-temperature and ν_T is a chemistry-dependent constant. For a linear polymer chain shown as follows



we have $L = N_0 l_0 \sin(\phi/2)$, where L, N_0, l_0, and ϕ are the contour length, the number of the chemical bonds, the average length of each chemical bond, and the angle between the two neighboring bonds in its chain backbone, respectively. On the other hand, from the definition of l and N, we have $L = l\,N$, so that eq 1 can be rewritten as

$$R_\Theta^{\ 2} = l\,L = l\,[l_0 \sin(\phi/2)]N_0 \tag{3}$$

with $N_0 = 2M_{\text{polymer}}/M_{\text{monomer}}$, where "2" accounts for the fact that each monomer produces two chemical bonds. Furthermore, in terms of the radius of gyration R_g we can define the swelling factor of an isolated polymer chain as

$$\alpha_g^{\ 2} = \frac{R_{g,T}^{\ \ 2}}{R_{g,\Theta}^{\ \ 2}} \tag{4}$$

where $R_{g,\Theta}^{\ 2} \equiv R_\Theta^{\ 2}$. The experimental results have shown that for a long polymer chain at $T \geq \Theta$ the swelling factor $\alpha_g^{\ 2}$ depends only on the scaling variable Z defined in eq 2. Within the accuracy of the first-order renormalized perturbation theory in the calculation, $\alpha_g^{\ 2}$ can be parametrized as

$$\alpha_g^{\ 2} = (1 + 1.01Z + 0.216Z^2)^{0.18} \tag{5}$$

In principle, eqs 1 and 2 hold only for monodisperse chains. In reality, we have to replace M_{polymer} with the weight-average molar mass $M_{w,\text{polymer}}$, i.e., $N_0 = M_{w,\text{polymer}}/M_{\text{monomer}}$. For a narrowly distributional polymer fraction, the residual polydispersity dependence can be ignored. By measuring the values of R_g of a set of narrowly distributed polymer standards with different molar masses around its Θ-temperature, we are able to obtain l on the basis of eq 3, Z on the basis of eqs 4 and 5, and ν_T on the basis of eq 2. The detail of the theory can be found elsewhere.[11]

Experimental Section

Sample Preparation. Deuterated polystyrene (DPS) samples were synthesized by the anionic polymerization of deuteriostyrene. Normal polystyrene (PS) standards were courtesy of Nanjing University, China. The weight-average molar masses (M_w) and polydispersity indexes (M_w/M_n) of DPS and PS used are listed in Table 1. Analytical grade cyclohexane (Aldrich) was used without further purification. The polymer concentration was in the range of $\sim 10^{-4}-10^{-3}$ g/mL. The solution was kept at 40 °C for at least 3 days to ensure a complete dissolution and was clarified with a 0.2 μm Millipore filter inside an oven to avoid precipitation. All the solutions were kept at 40 °C before the light-scattering experiment.

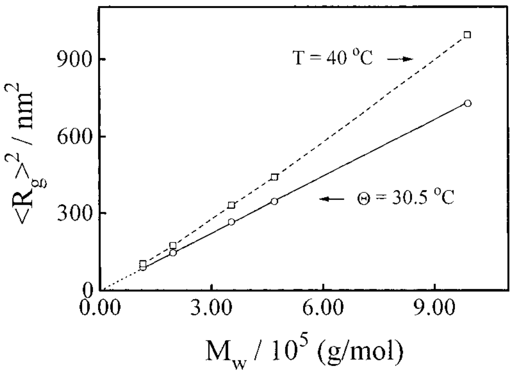


Figure 1. Molar mass dependence of the radius of gyration $\langle R_g\rangle^2$ of deuterated polystyrene (DPS) in cyclohexane respectively at the Θ-temperature (30.5 °C) and 40 °C, where the straight line represents a least-square fitting of $\langle R_g\rangle_\Theta^{\ 2} = 7.40 \times 10^{-4}\ M_w$.

Laser Light Scattering. The laser light scattering setup has been detailed before.[12] The incident laser light intensity was regulated with a beam attenuator (Newport M-925B) so that possible localized heating in the light-scattering cuvette can be avoided. The spectrometer was calibrated with toluene to make sure that the scattering intensity has no angular dependence. In static LLS, we were able to obtain the weight-average molar masses (M_w), the second virial coefficient (A_2), and the average radius of gyration ($\langle R_g\rangle$) from a Zimm plot which incorporates the concentration and angular dependence of the excess absolute scattering intensity, known as the Rayleigh ratio $R_{vv}(\theta)$, on a single grid.[13] In this study, the experimental uncertainties are less than 2%.

In dynamic LLS, the intensity−intensity time correlation function $G^2(t)$ was measured. For a pure diffusive relaxation, the cumulant analysis leads to the average transitional diffusion coefficient $\langle D\rangle$.[13,14] Since all the polymer samples used were very narrowly distributed, the first-order cumulant analysis of the measured $G^2(t)$ was sufficient to obtain an accurate value of $\langle D\rangle$. In this study, $q\langle R_g\rangle \sim 0.12$ and $C \sim 2 \times 10^{-4}$ g/mL, so that the extrapolations of $\langle D\rangle$ to $q \to 0$ and $C \to 0$ were not necessary. $\langle D\rangle$ was further converted to the hydrodynamic radius $\langle R_h\rangle$ by the Stokes−Einstein equation: $\langle R_h\rangle = k_BT/6\pi\eta\langle D\rangle$, where k_B is the Boltzmann constant and η is the viscosity of the solvent at the absolute temperature T. The detail of dynamic LLS can be found elsewhere.[14]

Results and Discussion

Figure 1 respectively shows the molar mass dependence of $\langle R_g\rangle^2$ for DPS in cyclohexane at the Θ-temperature (30.5 °C) and 40 °C, where the straight line shows a least-square fitting of $\langle R_g\rangle_\Theta^{\ 2} = 7.40 \times 10^{-4} M_w$. For DPS, $l_0 = 0.153$ nm, $\phi = 109.24°$, and $M_{\text{monomer}} = 112$ g/mol, so that $l_{\text{DPS}} = 0.331$ nm and $N = 0.377N_0$. l_{DPS} obtained here is larger than 0.297 nm reported by Schäfer because of a different definition of N_0.[9] Furthermore, from each α_g, i.e., $R_g(40\ °\text{C})/R_g(30.5\ °\text{C})$, we were able to calculate a corresponding $Z(R_g)$ on the basis of eq 5.

Figure 2 shows a plot of $Z(R_g)$ versus $N^{1/2}$ for DPS in cyclohexane at 40 °C, where the straight line represents a least-square fitting of $Z(R_g) = 0.0345N^{1/2}$. On the basis of eq 2, it leads to $\nu_{T,D} = 1.10$ which is smaller than 1.5 reported by Schäfer.[9] It should be noted that, besides the difference in the definition of N_0, Schäfer used only two values of A_2 to estimate ν_T. Therefore, our value of $\nu_{T,D} = 1.10$ should be more reliable. Following the same procedure, our calculation shows that $l_{\text{PS}} = 0.374$ nm and $\nu_{T,H} = 0.501$ for a normal PS chain in cyclohexane on the basis of the data of Miyaki and Fujita.[15] The fact that $l_{\text{DPS}} < l_{\text{PS}}$ and $\nu_{T,D} > \nu_{T,H}$ reveals that DPS and PS have different thermodynam-

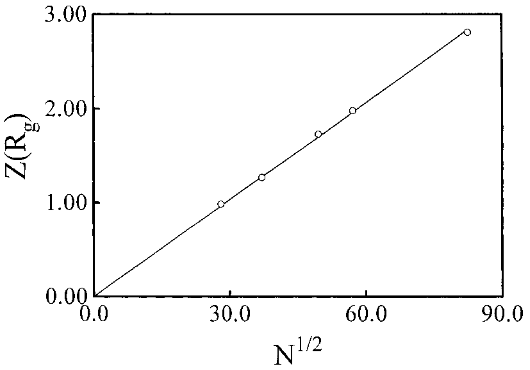


Figure 2. Plot of the scaling variable $Z(R_g)$ versus the square root of the number of segments $N^{1/2}$ for DPS in cyclohexane at 40 °C, where the straight line represents a least-square fitting of $Z(R_g) = 0.0345N^{1/2}$.

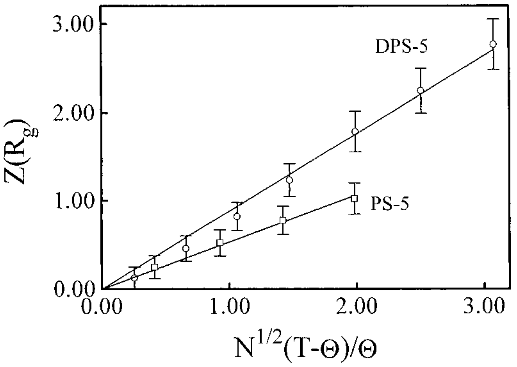


Figure 3. Plot of $Z(R_g)$ versus $N^{1/2}(T - \Theta)/\Theta$ respectively for DPS-5 and PS-5 in cyclohexane, where the error bars were estimated from the errors of $\langle R_g\rangle$ and the lines represent the least-square fitting of $Z_H(R_g) = 0.527N^{1/2}(T - \Theta)/\Theta$ and $Z_D(R_g) = 0.872N^{1/2}(T - \Theta)/\Theta$, respectively.

ics; namely, the smaller l_{DPS} indicates that at the Θ-temperature a DPS chain has a smaller conformation (i.e., coils more) than a PS chain with the same contour length, which suggests that at the Θ-temperature the intrachain interaction in DPS is stronger than that in PS; and on the other hand, the larger $\nu_{T,D}$ indicates that in a good solvent a DPS chain extends more than a PS chain for a given increase of the reduced temperature $(T - \Theta)/\Theta$. The thermodynamic difference between DPS and PS decreases as the reduced temperature increases. We further confirmed the difference between $\nu_{T,D}$ and $\nu_{T,H}$ by measuring the temperature dependence of $\langle R_g\rangle$ of a deuterated PS (DPS-5) and a normal PS (PS-5) with a similar molar mass around their corresponding Θ-temperatures.

Figure 3 shows a plot of $Z(R_g)$ versus $N^{1/2}(T - \Theta)/\Theta$, where the error bars were estimated from the errors of $\langle R_g\rangle$ and the lines respectively represent the least-square fitting of $Z_H(R_g) = 0.527N^{1/2}(T - \Theta)/\Theta$ and $Z_D(R_g) = 0.872N^{1/2}(T - \Theta)/\Theta$, resulting in $\nu_{T,H} = 0.527$, close to 0.501 calculated by using the data in ref 15, and $\nu_{T,D} = 0.872$, slightly smaller than 1.10 calculated from Figure 2. Therefore, the difference between $\nu_{T,D}$ and $\nu_{T,H}$ has been further demonstrated. Furthermore, we measured the hydrodynamic radii $\langle R_h\rangle$ of DPS in cyclohexane respectively at the Θ-temperature and 40 °C, and then followed an analysis similar to that used for $\langle R_g\rangle$ to investigate any possible difference between the hydrodynamics of DPS and PS.

Figure 4 respectively shows two plots of $\langle R_h\rangle^2$ versus M_w for DPS in cyclohexane at the Θ-temperature and 40 °C, where the straight line represents a least-square fitting of $\langle R_h\rangle_\Theta{}^2 = 3.72 \times 10^{-4}M_w$. We found that $l_D(R_h) = 0.165$ nm, and $l_D(R_g)/l_D(R_h) = 2.0$, much larger than 1.4, the ratio of $\langle R_g\rangle_\Theta/\langle R_h\rangle_\Theta$ for a normal linear polymer chain at the Θ-temperature.[12] Furthermore, each $\langle R_h\rangle_T/\langle R_h\rangle_\Theta$ leads to a corresponding $Z(R_h)$.

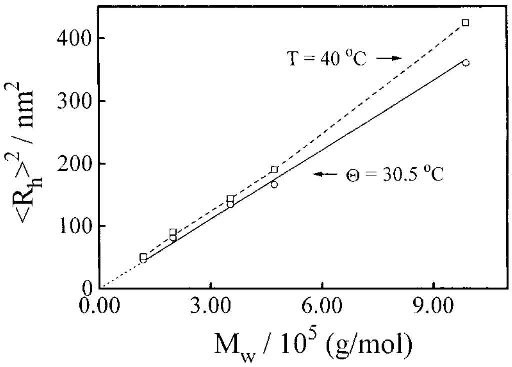


Figure 4. Plot of $\langle R_h\rangle^2$ versus M_w for DPS in cyclohexane respectively at the Θ-temperature and 40 °C, where the straight line represents a least-square fitting of $\langle R_h\rangle_\Theta{}^2 = 3.72 \times 10^{-4}M_w$.

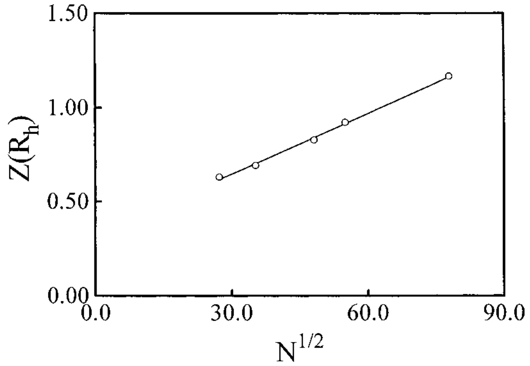


Figure 5. Plot of $Z(R_h)$ versus $N^{1/2}$ for DPS in cyclohexane at 40 °C, where the straight line represents a least-square fitting of $Z(R_h) = 0.319 + 0.0108N^{1/2}$.

Figure 5 shows a plot of $Z(R_h)$ versus $N^{1/2}$ for DPS in cyclohexane at 40 °C, where the straight line represents a least-square fitting of $Z(R_h) = 0.319 + 0.0108N^{1/2}$. In contrast to Figure 3, $Z(R_h)$ does not vanish at $T = \Theta$, which is understandable because $\langle R_h\rangle$ contains both the thermodynamic and hydrodynamic interactions. When the thermodynamic interaction vanishes at $T = \Theta$, the hydrodynamic interaction still exists. It is interesting to compare the temperature dependence of $\langle R_h\rangle$ of DPS and PS in cyclohexane around their corresponding Θ-temperatures and examine the effect of the deuteration on their hydrodynamics.

Figure 6 respectively shows the plots of $\langle R_h\rangle_T/\langle R_h\rangle_\Theta$ versus $(T - \Theta)/\Theta$ for DPS and PS in cyclohexane, in which the effects of the deuteration on their hydrodynamics can be clearly viewed. In the case of PS, $\langle R_h\rangle_T$ decreases as temperature increases, while in the case of DPS, $\langle R_h\rangle_T$ increases as temperature increases. This might be attributed to the fact that $\nu_{T,D} > \nu_{T,H}$, so that a DPS chain expands more than a PS chain for a given increase of the reduced temperature.[16]

Figure 7 respectively shows the plots of $\langle R_g\rangle_T/\langle R_h\rangle_T$ versus $(T - \Theta)/\Theta$ for DPS and PS in cyclohexane, where $\langle R_g\rangle_T/\langle R_h\rangle_T$ reflects the deuteration effects on both thermodynamics and hydrodynamics. The ratios of $\langle R_g\rangle_T/\langle R_h\rangle_T$ for both PS and DPS slightly increase as the reduced temperature increases, showing the expansion of polymer chains, which has been predicted by Schäfer and Baumgärtner.[16]

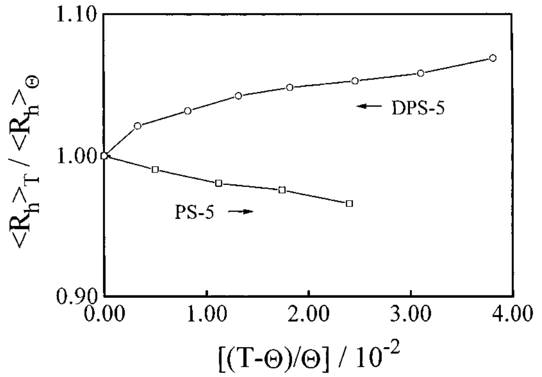


Figure 6. Plot of $\langle R_h\rangle_T/\langle R_h\rangle_\Theta$ versus $(T - \Theta)/\Theta$ respectively for DPS-5 and PS-5 in cyclohexane around their corresponding Θ-temperatures.

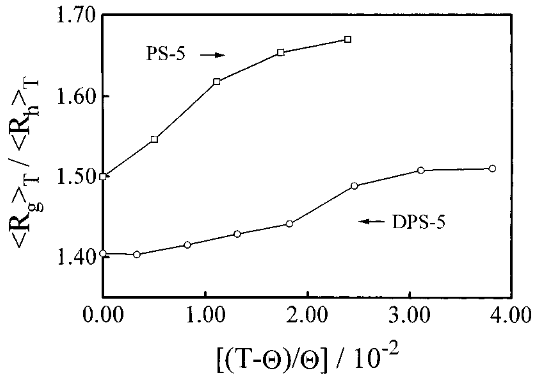


Figure 7. Plot of $\langle R_g\rangle_T/\langle R_h\rangle_T$ versus $(T - \Theta)/\Theta$ respectively for DPS-5 and PS-5 in cyclohexane around their corresponding Θ-temperatures.

In summary, our results indicate that the deuteration of a polystyrene chain increases its intrachain interaction in solution at the Θ-temperature so that it has a smaller conformation (i.e., coils more) than a PS chain with the same contour length. The deuteration also leads to a much larger chemistry-dependent constant ν_T, revealing that in a good solvent a deuterated polystyrene chain extends more than a normal polystyrene chain for a given reduced temperature $(T - \Theta)/\Theta$. To our knowledge, a reliable value of $\nu_T = 1.10$ for deuterated polystyrene has, for the first time, been reported, which provides a basis for further theoretical calculations. The difference in the thermodynamics of DPS and PS is also reflected in their hydrodynamics. Therefore, we have to examine the use of deuteration in neutron scattering and NMR, and reconsider the interpretation of the experimental results.

Acknowledgment. The financial support of this work by RGC (the Research Grants Council of the Hong Kong Government) Earmarked Grants CUHK 305/96P (A/C No. 2160063) is gratefully acknowledged.

References and Notes

(1) Zirkel, A.; Richter, D.; Pyckhout-Hintzer, W.; Fetters, L. J. *Macromolecules* **1992**, *25*, 954.
(2) Daoud, M.; Cotton, J. P.; Farnoux, B.; Jannink, G.; Sarma, G.; Benoit, H.; Duplessix, R.; Picot, C. *J. Chem. Phys.* **1976**, *65*, 1101.
(3) Richter, D; Farago B.; Fetters, L. J.; Huang, J. S.; Ewen, B.; Lartigue, C. *Phys. Rev. Lett.* **1990**, *64*, 1389.
(4) Sakurai, S.; Hasegawa, H.; Hashimoto, T.; Hargis, I. G.; Aggarwal, S. L.; Han, C. C. *Macromolecules* **1990**, *23*, 451.
(5) Graessely, W. W.; Krishnamoorti, R.; Balsara, N. P.; Fetters, L. J.; Lohre, D. J.; Schulz, D. N.; Sissano, J. A. *Macromolecules* **1993**, *26*, 1137.
(6) Galvin, M. E.; Heffner S.; Winey, K. I. *Macromolecules* **1994**, *27*, 3520.
(7) Hong, P. P.; Boerio, F. J.; Smith, S. D. *Macromolecules* **1994**, *27*, 596; *Macromolecules* **1993**, *26*, 1460.
(8) Strazielle, C.; Benoit, H. *Macromolecules* **1975**, *8*, 203.
(9) Schäfer, L. *Macromolecules* **1993**, *26*, 6425.
(10) Schäfer, L. *Macromolecules* **1984**, *17*, 1357.
(11) Des Cloizeaux, J.; Jannink, G. *Polymer in Solutions*; Clarendon Press: Oxford, 1990.
(12) Wu, C.; Zhou, S. *Macromolecules* **1995**, *28*, 8381.
(13) Chu, B. *Laser Light Scattering*, 2nd ed.; Academic Press: New York, 1991.
(14) Pecora, R. *Dynamic Light Scattering*; Plenum Press: New York, 1976.
(15) Miyaki, Y.; Einaga, Y.; Fujita, H. *Macromolecules* **1978**, *11*, 1180. Miyaki, Y.; Fujita, H. *Macromolecules* **1981**, *14*, 742.
(16) Schäfer, L.; Baumgärtner, A. *J. Phys.* **1986,** *47*, 1431.

MA9711046