Hydrogen Bonding of Methyl Red to Poly(methyl methacrylate) and Poly(vinyl acetate) in Toluene Solution: A Diffusion, Binding, and Simulation Study

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ABSTRACT: We investigated the hydrogen bonding of a small molecule to polymer chains by forced Rayleigh scattering, equilibrium binding, and computer simulation. Diffusion of 4-(4′-(dimethylamino)-phenylazo)benzoic acid (p-MR) was reported previously to be far more retarded in a toluene solution of poly(methyl methacrylate) (PMMA) or poly(vinyl acetate) (PVAc) than in a polystyrene solution due to the hydrogen bonding of the carboxylic hydrogen in p-MR with the carbonyl groups in PMMA or PVAc. In this study, we found that PVAc solution exhibits a more effective retardation of the p-MR diffusion than the PMMA solution despite their similar molecular structures. The difference in the p-MR diffusivity in PVAc and PMMA solutions could be attributed to the difference in binding efficiency of the probe dye onto the two polymers. In addition, the computer simulation calculation of the surface area of the carbonyl group of the polymer chains accessible for a small molecule to hydrogen bond showed a difference between the two polymers, which was consistent with the results of the diffusion and equilibrium binding studies.

Introduction

Hydrogen bonding has long been a subject of great interest due to its significant effect on various properties in chemical and biological systems. To understand the numerous physical and chemical phenomena caused by hydrogen bonding, it is necessary to consider the spatial configurations of the participating atoms forming a hydrogen bond.[1–3] A subtle difference in the molecular structure could give rise to a significant effect in the H-bonding characteristics.[4] It is not an easy task to elucidate the hydrogen-bonding effect in polymeric systems at the molecular level with currently available experimental techniques because a polymer chain has many internal degrees of freedom. With the recent advent of computer resources, various computer simulation methods such as energy minimization, molecular dynamics, and Monte Carlo method have been successfully applied to the investigation of synthetic and biological polymeric systems in which H-bonding interaction exists.[5–15] These methods allow visualization of the conformational characteristics of the polymer chains and the specific interactions of interest in the atomic level.

This study is concerned with the hydrogen-bonding effect on the molecular transport phenomena in the polymeric media. The motivation of this study in part stems from the extensive application of polymeric materials to the systems utilizing diffusion-controlled processes such as separation membranes and drug carriers. Hydrogen bonding affects the molecular transport behavior through polymeric media significantly as exemplified from a number of the experimental studies of diffusion or membrane permeation.[3,16–28] A good example is the diffusion of methyl red (MR) in semidilute toluene solutions of poly(methyl methacrylate) (PMMA) or poly(vinyl acetate) (PVAc).[19–26] Diffusion of MR is far more retarded in PVAc or in PMMA solutions than in polystyrene solutions at the equivalent polymer concentrations since PVAc and PMMA contain carbonyl groups that are capable of hydrogen bonding with the carboxylic hydrogen of MR. Furthermore, we found in this study that there is a clear difference in MR diffusivity between PVAc and PMMA solutions, indicating that the hydrogen-bonding abilities of the two polymers are distinguishable despite their similar molecular structures. To elucidate the effect on the diffusion of MR caused by this small structural difference in the polymer chains, we extended the experimental studies on the hydrogen-bonding capability of PMMA and PVAc to the equilibrium binding as well as computer simulation studies. For the equilibrium binding study, modified gel permeation chromatography (GPC) was employed to investigate the binding efficiency of MR to PVAc relative to PMMA. An example of the application of this method to the polymer solution systems was reported recently.[25] In addition, we attempted to verify the experimental results of diffusion and equilibrium binding studies at the molecular level by computer simulation methods.

Experiment

Materials. 4-(4′-(Dimethylamino)phenylazo)benzoic acid (p-MR) was used as a probe molecule for the diffusion and equilibrium binding studies in semidilute polymer solutions. p-MR was acquired from Tokyo Chemical Inc. and purified by recrystallization in methanol. Toluene, the solvent for both diffusion and equilibrium binding experiments, was used as received from Aldrich (HPLC grade). Polystyrene, PMMA, and PVAc were acquired from Miwon Petrochemical Co. and Aldrich, respectively. The average molecular weight and the molecular weight distribution were estimated by conventional GPC analysis relative to polystyrene standards. Molecular characteristics of the polymers used in this study are summarized in Table 1.

Forced Rayleigh Scattering. A forced Rayleigh scattering (FRS) apparatus used in this study has been described in detail elsewhere.[26] The 488 nm line of an Ar ion laser (Coherent,

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Table 1. Characteristics of the Polymers Used in This Study

polymers	M_w ($\times 10^3$)[a]	M_w/M_n	source
PS	276	2.43	Miwon Petrochemical
PMMA	77.6	2.01	Aldrich
PVAc[b]	85.6	1.13	Aldrich
PVAc[c]	159	2.98	Aldrich

[a] Determined by GPC relative to PS standards. [b] Used in the FRS experiments. [c] Used in the binding experiments.

model 90-3) was used for the writing beam, and the 632.8 nm line of a He−Ne laser (Melles Griot, 5 mW) was used for the reading beam. The temperature of the sample was regulated at 25.0 ± 0.1 °C by enclosing the sample cell with a copper block of which temperature is controlled by circulating a fluid from a bath/circulator (Lauda, RC6). Samples for FRS measurements were prepared gravimetrically by dissolving the polymers in dilute toluene solution of p-MR (∼0.01 mg/mL). After the complete dissolution of the polymers, solutions were filtered through Teflon membrane filters (Gelman, 0.2 μm pore) directly to 5 mm path length spectroscopic quartz cuvettes (Uvonic type 21-Q) for the FRS measurements. It was confirmed that the average molecular weight and the molecular weight distribution of polymers as well as the dye concentration do not affect the diffusivity of p-MR in this experimental condition.[20,21] In the FRS measurements, decay profiles of the diffracted light intensity showed a single-exponential decay, and the decay time constant, τ, was determined by fitting the decay signal to the following model function.

$$I_d(t) = [A \exp(-t/\tau) + B]^2 + C \tag{1}$$

where A is the amplitude of the diffracted optical field, B is the coherent background, and C is the incoherent background.[18,19,29−34] The diffusivity of p-MR was obtained from the slope of the $1/\tau$ vs q^2 ($=4\pi^2/d^2$) plot, where d is the spacing of the optical grating created by crossing the writing beam.

Equilibrium Binding Study. The apparatus for the equilibrium binding study was described previously.[25] The GPC system consists of an HPLC pump (LDC, ConstaMetric 3200), a six-port sample injector (Rheodyne 7125), a variable wavelength UV/vis absorption detector (TSP, Spectra 100), a refractive index (RI) detector (LDC, RefractoMonitor IV), and two PS gel columns (Shodex, KF-8025). The temperature of the column was maintained at 25 °C using a homemade column jacket connected to a bath/circulator (NESLAB, RTE-111). The eluent was a toluene solution of p-MR at the concentration of 0.01 mg/mL, which was the same concentration as the solution used in the FRS study. Injection samples were prepared by dissolving a polymer to be analyzed in the eluent and injected to a 100 μL loop of the injector. Concentration of the polymer in the injection sample was identical for both PVAc and PMMA at 7% (w/w). Under our experimental conditions, the binding characteristics were independent of the flow rate up to 1.0 mL/min, and the measurements were carried out at a flow rate of 0.5 mL/min.

p-MR is a photochromic dye to change its absorption spectrum depending on its photochemical state, which was affected by external light. We found that the most reproducible result was obtained when the wavelength of UV/vis detector was set at 382 nm, an isosbestic point of p-MR in toluene.[25] Another advantage of selecting the wavelength at 382 nm is that neither the polymers nor the solvent shows measurable absorption at the wavelength.

Conformational Analysis of Polymer. To build the equilibrium conformations of PMMA or PVAc chain, the distribution of torsion angles needs to be calculated first. The statistical weights of the rotational isomeric states (RIS) for PMMA and PVAc were obtained by the RIS Metropolis Monte Carlo (RMMC) method.[5,6,35] The RMMC calculation begins with a chain of an arbitrary conformation. In this study, the 20mers of PMMA and PVAc were built by random generation as an
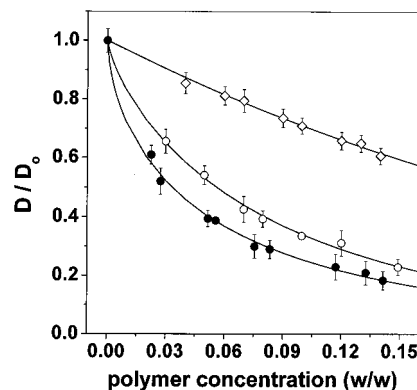

Figure 1. Diffusivities of p-MR in toluene solution of PS (◇), PMMA (○), and PVAc (●) as a function of the polymer concentration. The extent of retardation of p-MR diffusion is larger in the order of PVAc, PMMA, and PS. D_0 is the diffusivity of p-MR in pure toluene, and the experimental temperature was 25 °C. Solid lines are the fits to eq 2.

initial structure, and the simulation temperature was set at 300 K. The dielectric constant of toluene (2.378) was assigned for the calculation of the Coulombic interaction, which was the solvent in the FRS and equilibrium binding experiments. The potential energy of the initial conformation was preminimized by the conjugate gradient method. Then the torsion angles in this structure were allowed to vary, and the potential energy was calculated using the COMPASS (condensed-phase optimized molecular potentials for atomistic simulation studies) force field.[36] The potential energy of the new conformation was compared with the old conformation, and a decision was made whether to retain the change according to the Metropolis Monte Carlo algorithm.[5,6,35] This process is repeated for enough number of times, typically a few hundred thousand times, to yield an equilibrium conformation. With the torsion angle distribution obtained from the RMMC calculation, polymer chain models of PMMA and PVAc with fixed chain lengths were constructed by the RIS method. Then the hydrogen-bonding capabilities of PMMA and PVAc were compared by calculating the Connolly surface area. The Connolly surface is the van der Waals surface of the model accessible to a small molecule, and the Connolly surface area was calculated by rolling a spherical probe of a specified radius over the van der Waals surface that surrounds the carbonyl groups of the model.[37,38] To check the possible effect of the polymer chain length, three different chain lengths, 50, 100, and 150, in the number of the repeat units were examined. All the simulations were carried out on a SGI IRIX6.3 R10000 workstation using a CERIUS ^{2} release 3.8 package.[39]

Results and Discussion

Figure 1 shows diffusivities of p-MR in toluene solution of polystyrene (PS) (diamonds), PMMA (open circles), and PVAc (filled circles) as a function of the polymer concentration in toluene (w/w). The diffusivity, D, is normalized by the diffusivity measured in pure toluene, D_0. The error bars represent the uncertainties in the q^2 dependency of $1/\tau$ in the 95% confidence limit. As the polymer concentration increases, diffusion of p-MR is retarded due to the hydrodynamic as well as hydrogen-bonding interaction between the diffusant and the polymeric chains. The solid lines represent the best fit of the data to the stretched exponential form.[21−23,26,40−47]

$$D/D_0 = \exp(-\alpha C^\nu) \tag{2}$$

This equation evidently fits data very well. As reported earlier, the further retardation of the p-MR diffusion in the PMMA and PVAc solutions relative to the PS
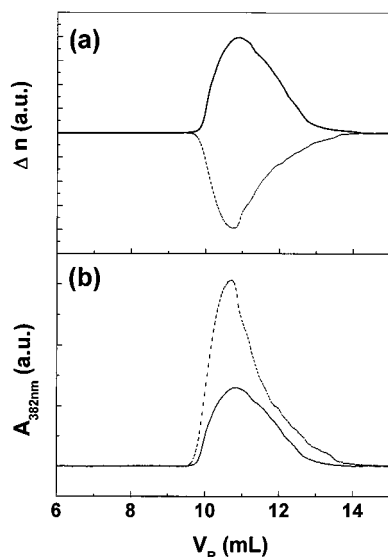
Figure 2. Modified GPC chromatograms of PMMA and PAVc recorded by (a) an RI detector and (b) a UV/vis detector at the wavelength of 382 nm. The eluent was toluene premixed with p-MR at the concentration of 0.01 mg/mL. The solid line is for PMMA, and the dashed line is for PVAc. Concentration of the polymer in the injection sample was identical for both PVAc and PMMA at 7% (w/w), and the injection volume was 100 μL.

solution is due to the hydrogen bonding between p-MR and PVAc or PMMA, which does not exist in the PS solution.[19–26] Another interesting point is the difference between the PVAc and the PMMA solution despite their similarity in the molecular structure.

It was previously confirmed that the retardation of the probe diffusion in PS/PMMA copolymer systems is governed by the binding efficiency of p-MR to the polymer chain.[25] To figure out whether the difference in the probe diffusion between PVAc and PMMA solution is also due to the difference in the binding of p-MR to the polymer chains, we carried out an equilibrium binding study. In Figure 2, the GPC chromatograms for PMMA (solid line) and PVAc (dashed line) obtained with the p-MR/toluene eluent system are shown. Parts a and b of Figure 2 show the chromatograms recorded by a RI detector and by a UV/vis absorption detector at the wavelength of 382 nm, respectively. Since we only needed to separate polymers from other small molecules, p-MR and the injection solvent, the pore size of the column was chosen to be small enough for the polymers to be eluted near the total exclusion limit. Therefore, the PMMA and PVAc used in this study are eluted at the similar retention volume (V_R) near the total exclusion limit despite their molecular weight difference. Because of the broad molecular weight distribution of the polymers and the heavy loading of the polymer samples, the polymer elution peaks span a rather large V_R range but are always completely separated from the injection solvent peak appearing at V_R near 20 mL. This enables us to compare the peak areas from which the binding constant of p-MR can be extracted without the interference of the system peak.

The chromatograms of each polymer recorded with the two different detectors show the elution peaks at the similar V_R, around 10–14 mL, and the similar peak shape, but different relative intensity. The peak area in the chromatogram recorded by a RI detector in Figure 2a represents the amount of the polymer injected as well

as the specific refractive index increment (dn/dc) of the polymer. The values of dn/dc in toluene are 0.0157 for PMMA (546 nm, 25 °C) and −0.020 for PVAc (560 nm, 25 °C).[48,49] The contribution of the bound p-MR is negligible in this case since the concentration of the dye is much lower than the polymers. PVAc shows an inverted peak due to the negative dn/dc of PVAc. Since the same amount of the polymers were injected and the |dn/dc| values of PVAc and PMMA are comparable to each other, the peak areas of the two polymers in the RI chromatograms are not much different. On the other hand, the peak areas recorded by a UV/vis detector are quite different for the two polymers in Figure 2b. As mentioned in the Experimental Section, p-MR is the only species in the system absorbing light at 382 nm wavelength. Therefore, the peak area in Figure 2b is the contribution of the excess p-MR bound to the polymer molecules. The larger peak area of PVAc samples than that of PMMA clearly shows a more preferential binding of p-MR to PVAc. This is consistent with the result of p-MR diffusion shown in Figure 1.

In our previous study on p-MR diffusion in PS/PMMA mixture and random copolymer systems, we found that the diffusivity was well correlated with the binding efficiency, i.e., the peak area (A). The plot of D_{PMMA}/D vs A/A_{PMMA} of the various PS/PMMA systems showed a master curve.[25] Since we are dealing with two polymer systems in this study, we do not have enough number of data points to make such a plot. However, it would be interesting to test whether the master curve made for PS/PMMA system works also for this system. Although not shown, the two ratios, $D_{PVAc}/D_{PMMA} = 0.79$ at 7% polymer concentration from Figure 1 and $A_{PMMA}/A_{PVAc} = 0.49$ from Figure 2b, fall on the master curve within experimental precision. Although it needs further experimental verification, the master curve appears to behave universally to correlate the ratio of the binding efficiency to the ratio of the diffusivity.

The stronger H-bonding ability of PVAc relative to PMMA may be understood intuitively from the fact that the carbonyl group of PVAc is more distant from the polymer chain backbone thus more exposed to external small molecules. To elucidate this difference from their molecular structure, we constructed a model of the PVAc and PMMA chains and calculated the Connolly surface area, which is the surface area of the carbonyl moiety accessible for a small molecule to interact with.[37,38] The polymer chain models were built by the RIS method using the probability distributions produced by the RMMC method. The probability distributions of the torsion angle for PMMA and PVAc calculated by the RMMC method are displayed in parts a and b of Figure 3, respectively. As shown in Figure 3, PVAc has a higher probability of the trans state than PMMA. This can be attributed to the α-methyl group in PMMA that makes the trans conformation have a higher energy relative to PVAc. The total area of the Connolly surface of a polymer chain is the van der Waals surface that surrounds the carbonyl group of the model, which is accessible to a probe of finite size. The radius of the rolling probe was chosen as 1.4 Å, which is the size of the water molecule. There are two reasons to choose the probe size of water molecule and not p-MR. First, the carboxylic hydrogen of p-MR forms hydrogen bonding, and it would be more reasonable to use not the size of a whole probe molecule but the size of the functional group forming the H-bond. Second, the computation
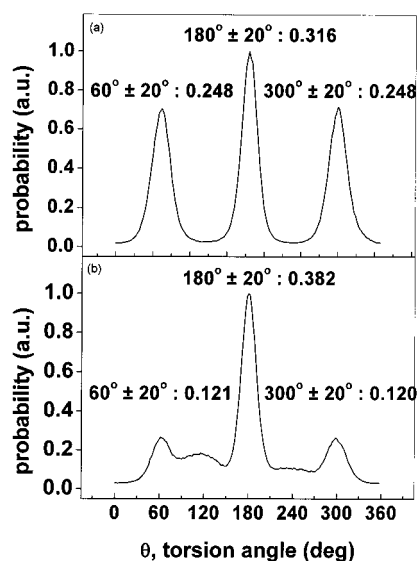
Figure 3. Normalized probability distribution of the torsion angles of (a) PMMA and (b) PVAc calculated by the RMMC method at 300 K. The 180° of the torsion angle stands for the trans state. The probabilities of the trans and gauche states over the ±20° around the central torsion angle of each state are shown in the plot.
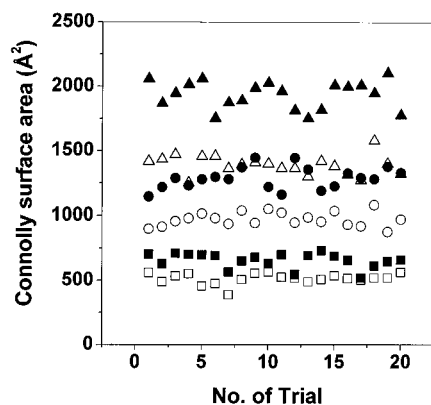

Figure 4. Connolly surface of the carbonyl groups in 50mer (squares), 100mer (circles), and 150mer (triangles) of PMMA (open symbols) and PVAc (filled symbols) chains. The Connolly surface was calculated for the probe size of 1.4 Å. PVAc constantly shows a larger Connolly surface than PMMA.

time strongly depends on the size of the probe, and it was not practical to use a larger size probe to generate a large amount of data. However, we confirmed that the relative magnitude of the Connolly surface area of the two polymers was not affected by the change of the probe size up to 7 Å.

Figure 4 displays the Connolly surface of the carbonyl groups in 50mer (squares), 100mer (circles), and 150mer (triangles) of PMMA (open symbols) and PVAc (filled symbols) chains. The Connolly surface area of PVAc is consistently larger than that of PMMA. The averages and standard deviations of the Connolly surface over the 20 independently obtained conformers are summarized in Table 2 for 50mer, 100mer, and 150mer. The total Connolly surface area is nearly proportional to the number of carbonyl groups, that is, the degree of polymerization. This simulation study indicates that the carbonyl groups in PVAc are exposed more than those in PMMA and more accessible for the small molecules to bind. It is consistent with the simple-minded expectation that the carbonyl group in PVAc chains have more conformational freedom than those in PMMA chains due

Table 2. Average Connolly Surface Area of Carbonyl Groups of the RIS Models of PMMA and PVAc

	PMMA ($Å^2$)	PVAc($Å^2$)
50mer	515 ± 42	657 ± 57
100mer	973 ± 56	1288 ± 84
150mer	1388 ± 75	1935 ± 108

to the longer distance from the chain backbone. In addition, higher probability of the trans state of PVAc should help the carbonyl groups to be more exposed for the small molecules to hydrogen bond. Accordingly, the lower diffusivity and higher binding constant of p-MR in the PVAc solution than in the PMMA solution are in good agreement with the simulation results.

In this simulation study we did not include the solvent molecules since including the solvent molecules demands a much longer calculation time. Instead, we included the dielectric constant of toluene for the calculation of the Coulombic interaction. Although it is necessary to include the solvent molecules for the quantitative results, the qualitative picture is unlikely to be affected significantly. In addition, the whole conformation of the polymer chains in a solvent should be affected by the excluded-volume effect.[50] However, the excluded-volume effect is a long-range interaction, and the hydrogen bonding would not be affected significantly by such a long-range conformational effect. In a short length scale, within a size of so-called thermal blob, it is known that a polymer chain has a conformation close to its unperturbed state.[51] Therefore, the result of the present simulation study is thought to provide a proper insight into the dependence of hydrogen bonding on the molecular structure of the polymer chains.

References and Notes

(1) Jeffrey, G. A.; Saenger, W. *Hydrogen Bonding in Biological Structures*; Springer: Berlin, 1991.

(2) Smith, D. A. Modeling the Hydrogen Bond In *ACS Symposium Series*; Comstock, M. J., Ed.; American Chemical Society: Washington, DC, 1993; Vol. 569.

(3) Stannett, V. Simple Gases. In *Diffusion in Polymers*; Crack, J., Park, G. S., Eds.; Academic Press: London, 1968.

(4) Park, H. S.; Oh, K. S.; Kim, K. S.; Chang, T.; Spiegel, D. R. *J. Phys. Chem. B* **1999**, *103*, 2355.

(5) Allen, M. P.; Tildesley, D. J. *Computer Simulation of Liquids*, 1st ed.; Oxford University Press: New York, 1987.

(6) Galiatsatos, V. Computational Methods for Modeling Polymers: An Introduction. In *Reviews in Computational Chemistry 6*; Lipkowitz, K. B., Boyd, D. B., Eds.; VCH: New York, 1995.

(7) Tamai, Y.; Tanaka, H.; Nakanishi, K. *Macromolecules* **1996**, *29*, 6750.

(8) Tamai, Y.; Tanaka, H.; Nakanishi, K. *Macromolecules* **1996**, *29*, 6761.

(9) Müller-Plathe, F.; van Gunsteren, W. F. *Polymer* **1997**, *38*, 2259.

(10) Choi, S. S.; Jang, J. H. *Polymer* **1998**, *39*, 5861.

(11) Bharadwaj, R. K.; Boyd, R. H. *Polymer* **1999**, *40*, 4229.

(12) Trommsdorff, U.; Tomka, I. *Macromolecules* **1995**, *28*, 6138.

(13) Liang, C.; Yan, L.; Hill, J.; Ewing, C. S.; Stouch, T. R.; Hagler, A. T. *J. Comput. Chem.* **1995**, *16*, 883.

(14) Hagler, A. T.; Huler, E.; Lifson, S. *J. Am. Chem. Soc.* **1974**, *96*, 5319.

(15) Sordo, J. A.; Sordo, T. L.; Fernández, G. M.; Gomperts, R.; Chin, S.; Clementi, E. *J. Chem. Phys.* **1989**, *90*, 6361.

(16) Lu, J. G.; Kong, L.; Chan, T. C. *J. Chem. Phys.* **1999**, *110*, 3003.

(17) Barrie, J. A. Warer in Polymers. In *Diffusion in Polymers*; Crack, J., Park, G. S., Eds.; Academic: London, New York, 1968.

(18) Xia, J. L.; Wang, C. H. *J. Chem. Phys.* **1988**, *88*, 5211.

(19) Huang, W. J.; Frick, T. S.; Landry, M. R.; Lee, J. A.; Lodge, T. P.; Tirrell, M. *AIChE J.* **1987**, *33*, 3.

(20) Lee, J. A.; Lodge, T. P. *J. Phys. Chem.* **1987**, *91*, 5546.

(21) Park, H. S.; Sung, J.; Chang, T. *Macromolecules* **1996**, *29*, 3216.

(22) Lee, J.; Park, K.; Chang, T.; Jung, J. C. *Macromolecules* **1992**, *25*, 6977.

(23) Sung, J.; Chang, T. *Polymer* **1993**, *34*, 3741.

(24) Spiegel, D. R.; Marshall, A. H.; Jukam, N. T.; Park, H. S.; Chang, T. *J. Chem. Phys.* **1998**, *96*, 190.

(25) Lee, H.; Chang, T. *Macromolecules* **1999**, *32*, 4147.

(26) Lee, J.; Park, T.; Sung, J.; Park, S.; Chang, T. *Bull. Korean Chem. Soc.* **1991**, *12*, 569.

(27) Slark, A. T.; Hadgett, P. M. *Polymer* **1999**, *40*, 4001.

(28) Hall, D. B.; Hamilton, K. E.; Miller, R. D.; Torkelson, J. M. *Macromolecules* **1999**, *32*, 8052.

(29) Léger, L.; Hervet, H.; Rondelez, F. *Macromolecules* **1981**, *14*, 1732.

(30) Kim, H.; Chang, T.; Yohanan, L.; Wang, L.; Yu, H. *Macromolecules* **1986**, *19*, 2737.

(31) Park, S.; Sung, J.; Kim, H.; Chang, T. *J. Phys. Chem.* **1991**, *95*, 7121.

(32) Johnson, C. S., Jr. *J. Opt. Soc. Am. B* **1985**, *2*, 317.

(33) Spiegel, D. R.; Sprinkle, M. B.; Chang, T. *J. Chem. Phys.* **1996**, *104*, 4920.

(34) Chapman, B. R.; Gochanour, C. R.; Paulaitis, M. E. *Macromolecules* **1996**, *29*, 5635.

(35) Metropolis, N.; Rosenbluth, A. W.; Rosenbluth, M. N.; Teller, A. H.; Teller, E. J. *J. Chem. Phys* **1953**, *21*, 1087.

(36) Sun, H. *J. Phys. Chem. B* **1998**, *102*, 7338.

(37) Connolly, M. L. *J. Appl. Crystallogr.* **1983**, *16*, 548.

(38) Connolly, M. L. *Science* **1983**, *221*, 709.

(39) *Cerius²*; Release 3.8 ed.; Molecular Simulation Inc.: San Diego, CA, 1998.

(40) Phillies, G. D. J.; Peczak, P. *Macromolecules* **1988**, *21*, 214.

(41) Chang, T.; Kim, H.; Yu, H. *Macromolecules* **1987**, *20*, 2629.

(42) Furukawa, R.; Arauz-Lara, J. L.; Ware, B. R. *Macromolecules* **1991**, *24*, 599.

(43) Park, I. H.; Johnson, C. S. J.; Gabriel, D. A. *Macromolecules* **1990**, *23*, 1548.

(44) Ullmann, G. S.; Ullmann, K.; Lindner, R. M.; Phillies, G. D. J. *J. Phys. Chem.* **1985**, *89*, 692.

(45) Phillies, G. D. J.; Brown, W.; Zhou, P. *Macromolecules* **1992**, *25*, 4948.

(46) Wattenbarger, M. R.; Bloomfield, V. A.; Bu, Z.; Ruzzo, P. S. *Macromolecules* **1992**, *25*, 5263.

(47) Rao, B.; Uemura, Y.; Dyke, L.; Macdonald, P. M. *Macromolecules* **1995**, *28*, 531.

(48) Huglin, M. B. Specific Refractive Index Increments of Polymers in Dilute Solution. In *Polymer Handbook*, 3rd ed.; Brandrup, J., Immergut, E. H., Eds.; John Wiley & Sons: New York, 1989; pp VII/432.

(49) van Krevelen, D. W. *Properties of Polymers*; Elsevier Science: Amsterdam, 1990.

(50) Yamakawa, H. *Modern Theory of Polymer Solutions*; Harper and Row: New York, 1971.

(51) de Gennes, P.-G. *Scaling Concepts in Polymer Physics*; Cornell University Press: Ithaca, NY, 1979.