Diffusion of Polystyrene Chains and Fluorescent Dye Molecules in Semidilute and Concentrated Polymer Solutions

Christopher A. Grabowski and Ashis Mukhopadhyay*

Department of Physics & Astronomy, Wayne State University, Detroit, Michigan 48201

Received May 7, 2008; Revised Manuscript Received June 18, 2008

ABSTRACT: Fluorescence correlation spectroscopy (FCS) experiments have been performed to measure the center-of-mass diffusion coefficient of fluorescently labeled polystyrene ($M_W = 8100$ g/mol) dissolved in polymer/toluene solutions above the overlap concentration. The diffusion coefficient was found to decrease by 2 orders of magnitude for a concentration change of 0.17−0.6 g/cm^3 at 34 °C. Less dramatic changes were observed at higher temperatures. The results are compared with the diffusion of free dyes in similar concentrated solutions. Vrentas−Duda free volume theory can explain the data reasonably well, from which the unit size of transport for the labeled macromolecule and the dye relative to the solvent is determined. The activation energy of diffusion was found to increase significantly as a function of concentration.

Introduction

The dynamics of polymers dissolved in a solvent can be classified in three separate regimes according to their concentration: dilute, semidilute, and concentrated. Polymers in dilute solutions are isolated from each other and adopt random coil configurations. The molecular weight of the polymer and the solvent viscosity solely impact polymer diffusion in the dilute regime. Polymer solutions that exceed a critical concentration c^* are classified as semidilute if the chains are not entangled. Once a solution reaches this situation, the dynamics are directly affected by polymer concentration. Polymer diffusion increases with concentration in this regime because the restoring forces due to osmotic pressure gradients become stronger at higher concentrations.[1,2] Even higher polymer concentrations can introduce topological constraints caused by entanglement. Polymers in concentrated solutions tend to experience a sharp decrease in diffusion because entanglement reduces the freedom of polymer chain movement at long length scales, which significantly alters chain dynamics.

The dependence of polymer diffusion on concentration has been treated theoretically using scaling arguments[1] and mean field theories.[3] Many experimental investigations on the diffusion of dilute and semidilute polystyrene solutions have supported their predictions. Small-angle neutron scattering[4] (SANS), light scattering,[5−8] optical beam deflection,[9] viscometry,[10] and more recently fluorescence correlation spectroscopy (FCS) techniques[11] have been used in this area of research. Polymer solutions in the concentrated regime, however, have not been as thoroughly studied. Highly concentrated polymer solutions limit the number of techniques that are capable of measuring their slow dynamics. The mass diffusion of concentrated polymer solutions has been previously investigated mainly using thermal diffusion forced Rayleigh scattering (TDFRS)[12,13] as well as static and dynamic light scattering.[14−19] These experiments report that the polymer mass diffusion reaches a maximum with concentration. Although polymers below a certain molecular weight will not entangle at any concentration, a decline in diffusion is still observed in some experiments.[12] This observation has been interpreted in terms of the increase of the local viscosity due to intersegmental friction. Characterization of the local friction coefficient as a function of concentration and temperature in a polymer solution is of significant importance in the area of polymer physics.

A complementary method in the investigation of polymer solution dynamics involves measuring the diffusion of small probe molecules and/or solvent molecules. In the concentrated regime, it can provide information about the local segmental motion of the macromolecule. Probe and solvent molecule diffusion in concentrated polymer solutions have been studied through FRS measurements,[20−23] depolarized Rayleigh scattering,[24] Taylor dispersion,[12] and powerful nuclear magnetic resonance (NMR)[25−27] techniques. In these experiments, both probe molecules and solvent molecules have shown Arrhenius behavior at all concentrations, and the activation energy rises in a nonlinear fashion for increasing concentration. Furthermore, the magnitude of the activation energy for both probe and solvent molecules has been found to be in good agreement with each other.[21,28] This increase in activation energy is caused by reduction in the free volume available to the diffusing molecules at high concentrations, and various free volume theories have been quite successful in interpreting these results.[20−23,28,29] While extensive experiments have been conducted measuring the diffusion of polymers and probes in polymer solutions, only a limited number of studies have directly compared their dynamics under the same experimental conditions.[27]

Fluorescence correlation spectroscopy is a recently developed experimental technique which has been widely used in the field of chemical biology but not as much in the field of polymer physics. A particular advantage of FCS is the use of ultralow concentrations of probe molecules, which perturbs the system minimally. In the following, we report the results of FCS measurements for diffusion coefficients of polymer chains and fluorescent dye molecules dissolved in polymer solutions above the overlap concentration. The center-of-mass diffusion coefficient of labeled polystyrene (PS) is compared with the diffusion of free dye (coumarin) over a wide range of temperatures and through a series of polymer concentrations. The activation energy of diffusion for PS and coumarin is then derived from this information. These results are analyzed in terms of Vrentas−Duda free volume theory and compared with previous experiments employing other methods.

Experimental Section

Method. FCS is a single molecule sensitive technique that monitors fluctuations in the emitted fluorescence of a sample.[30,31] These fluctuations arise from fluorescent dye molecules diffusing

---

* Corresponding author: e-mail ashis@wayne.edu, Tel 313-577-2775, Fax 313-577-3932.

10.1021/ma801035n CCC: $40.75

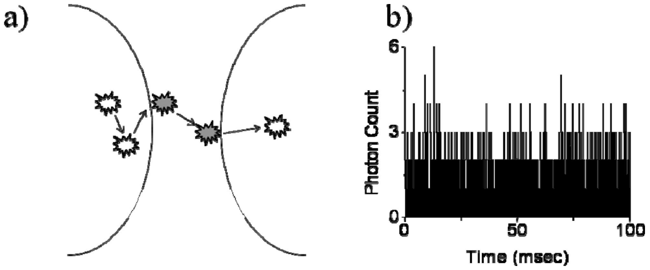

Figure 1. Experimental scheme: (a) a focused femtosecond laser causes two-photon excitation of fluorophores within a cylindrical volume of dimensions $\omega_0 \sim 0.58$ μm and $z_0 \sim 2$ μm; (b) the diffusion of dye molecules in and out of the laser focus causes emitted fluorescence to fluctuate with time. At any given instant, the fluorescent signal resulted from 1 to 5 dye molecules.

in and out of a laser focus that occupies an ultrasmall (~1 fL) volume element (Figure 1). Samples in these experiments were prepared so that between 1 and 5 dye molecules would occupy the focus at a given instant. By calculating the autocorrelation function of the fluorescence fluctuation intensity F, $G(\tau) \equiv \langle \delta F(t)\delta F(t+\tau)\rangle / \langle \delta F(t)\rangle^2$, and by choosing a suitable model to analyze it, the rate of dynamic process is obtained. The fluctuations of fluorescence counts in these experiments are caused by translational diffusion of dye molecules. The translational diffusion coefficient (D) can be determined from the autocorrelation function by using the relation $G(\tau) = G(0)/(1 + 8D\tau/\omega_0^2)(1 + 8D\tau/z_0^2)^{1/2}$. Here, $G(0)$ is the autocorrelation function magnitude at time lag $\tau = 0$ and is inversely proportional to the number of fluorophores in the laser focus. The beam width has been determined through calibration experiments of the dye fluorescein, which has a known diffusion coefficient of ~300 μm^2/s in water. In water we determined $\omega_0^{\text{water}} \approx 0.37$ μm. By using the known viscosity of toluene ($\eta \approx 0.59$ cP), we estimated by employing the Stokes–Einstein relation that $D \approx 510$ μm^2/s for fluorescein in toluene. By using this value for D, we determined that the beam width in toluene $\omega_0^{\text{toluene}} \approx 0.58$ μm. All solutions were prepared in toluene, so all subsequent autocorrelation analysis considers $\omega_0 = \omega_0^{\text{toluene}}$. The difference in beam width values for water and toluene in FCS experiments has been reported previously.[32]

FCS experiments were performed by a two-photon excitation of fluorescence. A femtosecond Ti–sapphire laser (Mai Tai, Spectra-Physics) generates 800 nm wavelength laser pulses of width 100 fs at a repetition rate of 80 MHz. The excitation power at the sample was kept less than 1 mW to avoid dye photobleaching and heating of the sample. A Zeiss inverted microscope (Axiovert S200TV, Carl Zeiss) served as the operational platform for the experiment. The laser beam was passed through an objective lens (63×, NA = 0.75) in order to generate a very small excitation volume within the sample solution. Fluorescence is collected through the same objective and detected by a pair of single-photon counting modules (Hamamatsu). The photon counting output is recorded and analyzed by an integrated FCS data acquisition system (ISS, IL). Temperature-based measurements were conducted by placing a sample cell holding the polymer solution into a cell holder whose temperature is regulated by a commercial proportional-integral-derivative (PID) temperature controller (Lakeshore). This setup provided a temperature stability of ±50 mK for over 3 h. The temperature was allowed to stabilize for 2 h before each FCS measurement, and each autocorrelation curve was averaged for ~30 min.

Sample Preparation. Polystyrene was chosen for these experiments because fluorescein-labeled samples of PS with low polydispersity ($M_w/M_n = 1.05$) are available for purchase commercially. We have performed photon counting histogram analysis on samples containing free fluorescein and fluorescein-labeled polymers. From these experiments, it has been determined that the molecular brightness (average number of detected photons per second per molecule) for both samples is very similar. This implies each labeled polymer has approximately one dye attached. A stock solution of 50 nM fluorescein-labeled PS (Polysciences, $M_W = 8100$ g/mol) in toluene was first prepared. Unlabeled PS (Polymer Source, $M_W = 8100$ g/mol) was then added in the solution to reach the desired concentration. A digital balance with a resolution of 1 mg was used. Concentrations investigated in this experiment ranged from 0.17 g/cm^3 up to 0.6 g/cm^3. The overlap concentration for the samples was estimated by using the relationship $c^* = [\eta]^{-1}$, where η is the intrinsic viscosity.[33] We determined that $c^* = 0.07$ g/cm^3; so all concentrations studied in our experiments are above the overlap concentration. As entanglement molecular weight of PS is 18 000 g/mol, which is ~170 monomers, entanglement is not possible at any concentration in our experiment.[27] Diffusion studies of free probe molecules were performed with the fluorescent dye coumarin 480 (Exciton), and the samples were prepared in the same manner as described earlier. The dyes used in these experiments maintained high photostability, as only minor photobleaching was observed (<5% decrease in fluorescent counts) over the course of each experiment. All measurements were performed in a sealed glass cell maintained at a constant temperature during the experiment.

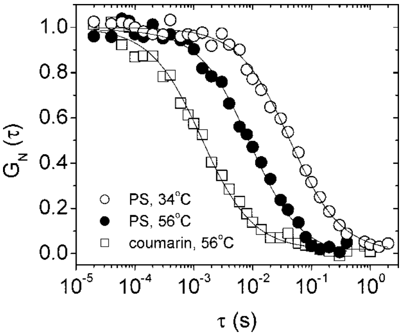

Figure 2. Normalized autocorrelation functions (ACFs) of fluorescein-labeled polystyrene (PS) ($M_W = 8100$ g/mol), diffusing through a PS solution of concentration 0.6 g/cm^3, taken at 34 and 56 °C (open and filled circles, respectively). An ACF of free dye coumarin 480 (open squares) diffusing through a 0.6 g/cm^3 PS solution, taken at 56 °C, is also shown. All ACFs can be successfully fitted with single diffusion time, yielding D_{PS} (34 °C) = 0.91 μm^2/s, D_{PS} (56 °C) = 4.54 μm^2/s, and D_{dye} (56 °C) = 29.7 μm^2/s.

Results and Discussion

Figure 2 displays representative autocorrelation functions collected by FCS. Intensity–intensity autocorrelation functions were calculated from the time series fluctuations of emitted fluorescence and plotted versus logarithmic time lag. As temperature is increased from 34 to 56 °C, the diffusion coefficient (D) of fluorescein-labeled PS in a 0.6 g/cm^3 toluene solution increases from 0.91 to 4.54 μm^2/s. The free dye coumarin diffusing through the same polymer concentration has a higher D of 29.7 μm^2/s at 56 °C. Each autocorrelation function calculated in our experiments fits well with a single parameter, namely the diffusion coefficient, which suggests that diffusing polymers and dye molecules obey homogeneous dynamics even in concentrated polymer solutions. This is expected even for the samples with the highest concentration, as the glass transition temperature of the mixture was well below the measurement temperatures.

Figure 3 shows the concentration dependence of the diffusion coefficient for coumarin (inset) and labeled PS at two temperatures, 34 and 56 °C, for polymer concentrations ranging from 0.17 to 0.6 g/cm^3. A steep decline in the diffusion of PS, almost by 2 orders of magnitude, occurs in this concentration range. The diffusion of dye molecules was less sensitive to PS concentration changes, especially for higher temperatures. An FCS experiment[11] conducted in the dilute and semidilute regimes has reported a power law dependence of polymer diffusion coefficient for concentrations ($D \sim c^{-1.75}$) above c^*. This originates from the reptation of entangled polymer chains.

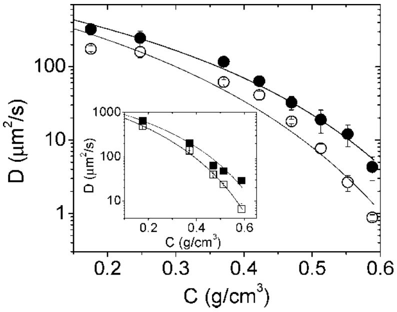

Figure 3. Concentration dependence on the diffusion coefficient for fluorescein-labeled PS at 34 °C (open circles) and 56 °C (filled circles). The curve fits are given according to the Vrentas−Duda equation with fitting parameter $\xi_{\text{polymer,s}} = 2.70$ for 34 °C and 2.42 for 56 °C. The inset shows concentration dependence of the diffusion coefficient for coumarin at 34 °C (open squares) and 56 °C (filled squares). The fitting parameters here are $\xi_{\text{probe,s}} = 2.18$ for 34 °C and 1.97 for 56 °C.

In our experiments, we did not observe such power law because the PS chains under investigation are too short to undergo entanglement even at a very high concentration. For polymers with molecular weights similar to our measurements, Rauch and Kohler[12] measured a 3 order of magnitude decrease in the diffusion of PS in toluene for a concentration increase of 0.2 to 0.8 g/cm^3 at 22 °C. Their results can be explained qualitatively in terms of approach toward the glass transition temperature (T_g) as the macromolecular concentration in the solution is increased. At a given temperature as the polymer concentration is increased, the system is effectively brought close to T_g, resulting in a dramatic slowdown of diffusion. Our results as well as results of ref 12 seem to be in disagreement with previous dynamic light scattering experiments by Zhang et al. using the same system and with similar molecular weight of polymer.[9] They have observed an increase in the collective diffusion coefficient of PS as the concentration of the solution is increased from 0.01 to 0.5 g/mL. It is important to note here that light scattering experiments measure mutual or cooperative diffusion coefficient, while FCS measurements measure the center-of-mass diffusion or self-diffusion coefficient. Doi and Edwards have previously demonstrated[3] that the concentration dependence of self-diffusion and mutual diffusion coefficients are different. Furthermore, the mutual diffusion coefficient of polystyrene in toluene has been experimentally shown to increase with increasing concentration, whereas the self-diffusion of polystyrene decreases.[34]

Additional insight into the transport processes in the polymer solution was obtained by measuring the temperature dependence of diffusion coefficient for coumarin and PS, which have been displayed in Figure 4. While some previous investigations have suggested that diffusion has a Vogel−Fulcher dependence on temperature,[15] the small temperature ranges in our investigation allow straight-line Arrhenius fits. Arrhenius behavior has been observed in previous experiments for both solvent molecules and dye molecules in concentrated polymer solutions,[21,28] when the experiments were performed at temperatures much higher the glass transition temperature of the solution. Even for the highest concentrated sample, all of our measurements were taken at least 100 °C above T_g of the mixture, which can be estimated by employing the Fox equation.[35] From an Arrhenius plot, we can determine the activation energy of diffusion by using $D = D_0 \exp(-E_A/k_BT)$. The activation energies of coumarin and fluorescein-labeled PS versus concentration are presented in Figure 5. At a low polymer concentration, we determined activation energy for coumarin ≈9.6 kJ/mol, which is close to the activation energy for neat toluene,[24] as well as coumarin diffusing through a Newtonian fluid.[29] Furthermore, at low concentrations E_A increases slowly, followed by a sharp increase at a high polymer concentration for both systems. This behavior is qualitatively similar to previous measurements of solvent self-diffusion and diffusion of small probe molecules through concentrated polymer solutions.

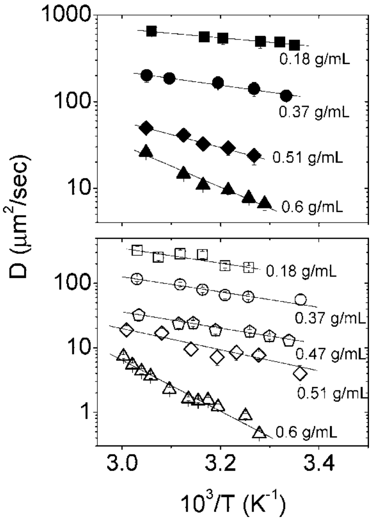

Figure 4. Temperature dependence of the diffusion coefficient for the free dye coumarin (top) and fluorescein-labeled PS (bottom), dissolved in varying concentrations of PS in toluene. In the temperature regime investigated, the data obey the Arrhenius equation (straight line fits). For clarity purposes, data for polymer diffusion at concentrations 0.25, 0.42, and 0.55 g/mL and dye diffusion at 0.47 g/mL have been omitted in this plot.

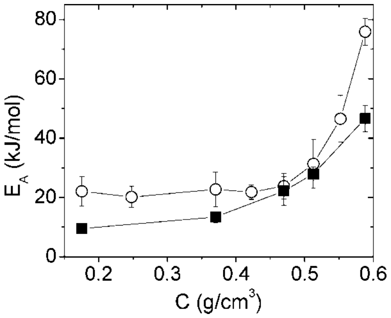

Figure 5. Activation energy (E_A) of the free dye coumarin (filled squares) and fluorescein-labeled PS (open circles) plotted as a function of PS concentration. E_A increases sharply above a concentration of 0.5 g/cm^3.

The complementary measurements of free dye and polymer mobility as performed in our experiments can be used to compare the frictional drag effective at the length scale of the size of one polymer segment and chain as a whole. In the context of free-volume theories, the friction coefficient is a strong function of concentration due to the dependence of free volume on concentration. Vrentas−Duda theory is the most successful among the free volume theories predicting the diffusion of solvent as well as small probe molecules as a function of concentration.[25,29] For negligible probe weight fraction in the mixture, it predicts the solvent diffusion coefficient, D_s, as

$$\ln\left(\frac{D_s}{D_{s0}}\right) = \left\{\left[\frac{-\gamma(\omega_s \hat{V}_s^* + \omega_p \xi_{s,p} \hat{V}_p^*)}{(\omega_s K_{1s}(T - T_{gs} + K_{2s}) + \omega_p K_{1p}(T - T_{gp} + K_{2p})}\right] + \frac{\gamma \hat{V}_s^*}{K_{1s}(T - T_{gs} + K_{2s})}\right\}$$

where ω_i is the weight fraction of component i ("s" for solvent and "p" for polymer), $\hat{V}_i^*$ is the specific free volume, K_{1i}/γ and $K_{2i} - T_{gi}$ are the free volume parameters for component i and

T_{gi} is its glass transition temperature. The quantity $\xi_{s,p}$ is the ratio of the jumping unit size of solvent to a polymer jumping unit (≈ monomer segment). The diffusion of the free dye (D_{probe}) and the labeled-polymer (D_{poly}) are related to the solvent diffusion coefficient through $\ln(D_{probe}/D_{probe,0}) = \xi_{probe,s} \ln(D_s/D_{s0})$, and $\ln(D_{polymer}/D_{polymer,0}) = \xi_{polymer,s} \ln(D_s/D_{s0})$. In theory, the quantity $\xi_{probe(polymer),s}$ represents the probe (polymer) jumping unit size relative to the solvent. The free volume parameters for PS-toluene system have been taken from ref 23. The solid lines through the data points in Figure 3 show the least-squares fitting, from which we determined $\xi_{probe,s} \approx 2.18$ and $\xi_{polymer,s} \approx 2.70$ at 34 °C. ξ decreases by ≈10% when the temperature is changed to 56 °C. It is interesting to note that though the molecular weight of polymer is ≈30 times bigger than the dye, the size of the unit of motion for polymer is only 20% higher. Following refs 20 and 22, we can write, $\xi_{polymer,s}/\xi_{probe,s} = (V^*_{polymer}/V^*_{probe})(M_{j,polymer}/M_{j,probe})$, where $M_{j,i}$ is the molecular weight of the jumping unit of the component i. We can estimate $V^*_{polymer} \approx 0.94$ cm^3/g and $V^*_{probe} \approx 0.78$ cm^3/g from refs 21 and 36, respectively, which gives $M_{j,polymer}/M_{j,probe} \approx 1.03$. By assuming that the probe jumps as a whole, $M_{j,probe} = 255$ g/mol, the molecular weight of coumarin. This would imply that $M_{j,polymer} \approx 263$ g/mol. Since the molecular weight of a PS monomer is 104 g/mol, the results indicate that polymer jumping unit is roughly equal to 2−3 times the single monomer unit. This value is close to the jumping unit size for a polymer obtained from independent forced Rayleigh scattering measurements.[21]

Conclusions

To summarize, the temperature dependence of the center-of-mass diffusion for fluorescently labeled PS and free dye coumarin was investigated in PS/toluene solutions above the overlap concentration. The diffusion was dramatically slowed at higher concentrations, which can be explained with increase in local viscosity due to the decrease in free volume. By fitting the data with the Vrentas−Duda free volume theory, we have determined the unit size of transport for polymer and free dyes in the solution. The activation energy of diffusion increases dramatically at higher macromolecular concentration.

Acknowledgment. is made to the donors of the American Chemical Society Petroleum Research fund (PRF # 44953-G5) and to the National Science Foundation through Grant DMR-0605900 for support of this research. A.M. also acknowledges the support from Research Corporation.

References and Notes

(1) de Gennes, P. G. *Scaling Concepts in Polymer Physics*; Cornell University Press: Ithaca, NY, 1979.
(2) Wang, C. H. *J. Chem. Phys.* **1991**, *95*, 3788.
(3) Doi, M.; Edwards, S. F. *The Theory of Polymer Dynamics*; Clarendon Press: Oxford, 1986.
(4) Daoud, M.; Cotton, J. P.; Farnoux, B.; Jannink, G.; Sarma, G.; Benoit, H.; Duplessix, R.; Picot, C.; de Gennes, P. G. *Macromolecules* **1975**, *8*, 804.
(5) Nemoto, N.; Makita, Y.; Tsunashima, Y.; Kurata, M. *Macromolecules* **1984**, *17*, 2629.
(6) Wiltzius, P.; Haller, H. R.; Cannell, D. S.; Schaefer, D. W. *Phys. Rev. Lett.* **1984**, *53*, 834.
(7) Li, J. F.; Li, W.; Huo, H.; Luo, S. Z.; Wu, C. *Macromolecules* **2008**, *41*, 901.
(8) Yuan, G. C.; Wang, X. H.; Han, C. C.; Wu, C. *Macromolecules* **2006**, *39*, 3642.
(9) Zhang, K. J.; Briggs, M. E.; Gammon, R. W.; Sengers, J. V.; Douglas, J. F. *J. Chem. Phys.* **1999**, *111*, 2270.
(10) Colby, R. H.; Fetters, L. J.; Funk, W. G.; Graessley, W. W. *Macromolecules* **1991**, *24*, 3873.
(11) Liu, R.; Gao, X.; Adams, J.; Oppermann, W. *Macromolecules* **2002**, *38*, 8845.
(12) Rauch, J.; Kohler, W. *Phys. Rev. Lett.* **2002**, *88*, 185901.
(13) Rauch, J.; Kohler, W. *J. Chem. Phys.* **2003**, *119*, 11977.
(14) Patterson, G. D.; Jarry, J. P.; Lindsey, C. P. *Macromolecules* **1980**, *13*, 668.
(15) Koch, T.; Strobl, G.; Stuhn, B. *Macromolecules* **1992**, *25*, 6255.
(16) Brown, W.; Nicolai, T. *Macromolecules* **1994**, *27*, 2470.
(17) Jian, T.; Vlassopoulos, D.; Fytas, G.; Pakula, T.; Brown, W. *Colloid Polym. Sci.* **1996**, *274*, 1033.
(18) Nicolai, T.; Brown, W. *Macromolecules* **1996**, *29*, 1698.
(19) Svanberg, C.; Uematsu, T.; Berntsen, P.; Jacobsson, P. *J. Chem. Phys.* **2007**, *126*, 051103.
(20) Frick, T. S.; Huang, W. J.; Tirrell, M.; Lodge, T. P. *J. Polym. Sci., Part B: Polym. Phys.* **1990**, *28*, 2629.
(21) Landry, M. R.; Gu, Q. J.; Yu, H. *Macromolecules* **1988**, *21*, 1158.
(22) Wisnudel, M. B.; Torkelson, J. M. *Macromolecules* **1996**, *29*, 6193.
(23) Rauch, J.; Hartung, M.; Privalov, A. F.; Kohler, W. *J. Chem. Phys.* **2007**, *126*, 214901.
(24) Floudas, G.; Steffen, W.; Fischer, E. W.; Brown, W. *J. Chem. Phys.* **1993**, *99*, 695.
(25) Chekal, B. P.; Torkelson, J. M. *Macromolecules* **2002**, *35*, 8126.
(26) Gisser, D. J.; Johnson, B. S.; Ediger, M. D.; von Meerwall, E. D. *Macromolecules* **1993**, *26*, 512.
(27) von Meerwall, E. D.; Amis, E. J.; Ferry, J. D. *Macromolecules* **1985**, *18*, 260.
(28) Pickup, S.; Blum, F. D. *Macromolecules* **1989**, *22*, 3961.
(29) Waggoner, R. A.; Blum, F. D.; Macelroy, J. M. D. *Macromolecules* **1993**, *26*, 6841.
(30) Pristinski, D.; Kozlovskaya, V.; Sukhishvili, S. A. *J. Chem. Phys.* **2005**, *122*, 014907.
(31) Zhao, J.; Granick, S. *Macromolecules* **2007**, *40*, 1243.
(32) Zettl, H.; Häfner, W.; Böker, A.; Schmalz, H.; Lanzendörfer, M.; Müller, A. H. E.; Krausch, G. *Macromolecules* **2004**, *37*, 1917.
(33) Brandrup, J.; Immergut, E. H.; Grulke, E. A.; Abe, A.; Bloch, D. R. *Polymer Handbook*, 4th ed.; John Wiley & Sons: New York, 2005.
(34) Cosgrove, T.; Sutherland, J. M. *Polymer* **1983**, *24*, 534.
(35) Fox, T. G.; Loshaek, S. *J. Polym. Sci.* **1955**, *15*, 371.
(36) www.chemspider.com.

MA801035N