Macromolecules **1996,** *29,* 6531−6534

Polymer Mobility in Thin Films

B. Frank and A. P. Gast

Department of Chemical Engineering, Stanford University, Stanford, California 94305

T. P. Russell,*,† H. R. Brown,‡ and C. Hawker

IBM Almaden Research Center, San Jose, California 95120-6099

Received May 21, 1996⊗

ABSTRACT: We present results from a diffusion study of polymer chains in thin films, in which the mobility of chains labeled with a fluorescent dye in a matrix of unlabeled chains has been measured using fluorescence recovery after patterned photobleaching. The results presented here indicate that there is a substantial decrease in the lateral diffusion coefficient for films thinner than ~1500 Å.

Introduction

The structure and properties of polymers at interfaces are critical in many scientific and technical applications, including adhesion, interdiffusion, and friction.[1−6] Many of these properties are affected by the mobility of the polymer. Experiments[6−13] indicate that the mobility of polymer chains in the vicinity of a surface or interface may be perturbed. Near a free surface, the mobility for lower molecular weight polymers is increased over that in the bulk, but higher molecular weight polymers exhibit no change in mobility.[10−12] Near a solid boundary, the interactions of the polymer chain with the solid may retard the chain mobility. Despite indirect evidence and significant recent interest,[13] there have been no direct studies on the extent to which a free surface, a hard boundary, or confinement alters the lateral motion of polymer chains. By studying polymer mobility in thin films, as opposed to the bulk, the influence of the interfaces on the system as a whole is enhanced, and the role of the interface in modifying the mobility of a polymer can be addressed.

In this study, the mobility of polymer chains has been examined using fluorescence recovery after patterned photobleaching (FRAPP). Dye-labeled molecules are bleached over selected regions, removing the chromophore locally, and the diffusion of the unbleached molecules into the bleached area is measured. This technique has been used by several other groups to explore diffusion in bulk polymer systems.[14−18] Here, the diffusion of a model polymer, polystyrene (M_w = 38 000), labeled with a fluorescent dye was measured in a matrix of unlabeled chains (M_w = 31 000). The results indicate that there is a substantial decrease in the diffusion coefficient for films with thicknesses less than ~1500 Å. These results are discussed in light of findings by other authors and in terms of the fundamental distance scales of the molecule.

Experimental Section

Polymers. The experiment required the synthesis of controlled, narrow molecular weight distribution polystyrene, with a single chain end labeled with a fluorescent chromophore. The chromophore of choice was a 7-nitrobenzofurazan group due to its absorption of light at 488 nm (one of the lines of an argon ion laser). To minimize perturbations to the configuration of the polymer, only a single fluorescent group was attached to one of the chain ends.

The synthetic approach to the appropriate amino-substituted polystyrenes utilized the recently developed concept of "living" free radical polymerization[19,20] followed by functionalization of the amino group to give the corresponding fluorescently tagged polymer (Scheme 1). Reaction of the *t*-Boc-protected (*N*-methylamino)phenol, **1**, with the bromo-substituted TEMPO derivative, **2**, gives the functionalized unimolecular initiator, **3**, in 72% yield after purification by flash chromatography. Polymerization of styrene by **3** under standard "living" free radical polymerization conditions, 123 °C for 48 h, then gives the functionalized polystyrene, **4**, where a single chain end bears a protected amino group. The molecular weight of **4** can be accurately controlled by the number of equivalents of styrene per equivalent of initiator, **3**. In our case, reaction of **3** with 350 equiv of styrene produced a monoamino-terminated polystyrene, **4**, with a M_w = 38 000 and a polydispersity of 1.32. Deprotection of the *t*-BOC group with trifluoroacetic acid followed by reaction with 4-chloro-7-nitrobenzofurazan (NBD-Cl) produced the desired fluorescently tagged polymer, **5**. No discernible change in the molecular weight or polydispersity of the polymer was observed on deprotection and functionalization, while UV−vis spectroscopy showed efficient functionalization of the chain ends.

The tagged polystyrene (TPS) was mixed with an untagged polystyrene (PS), M_w = 31 000 and polydispersity 1.03 (Polymer Laboratories Ltd.), and dissolved in toluene. The solutions ranged from 1 to 10% polymer by weight, with 12−100% of the polymer having tagged ends. Larger fractions of TPS were necessary for lower total polymer concentrations (thinner films) in order to obtain films with fluorescent signals significantly above the background. No measurable changes in the diffusion coefficients were found for similar films as a function of the fraction of TPS, indicating that the diffusion coefficient measured is independent of the fraction of the sample composed of TPS.

Substrates. The substrates were quartz disks with lithographically fabricated masks of chrome lines, used to create the bleaching pattern for the fluorescence experiment. After evaporating 750 Å of chrome onto the substrate, we spun a photoresist on the chrome produced lines in the photoresist through contact printing. By etching the chrome from between the lines, this pattern was transferred to the chrome, and the photoresist was removed. The resulting sample as measured by AFM had 2 μm wide chrome lines, ~750 Å high, spaced 2 μm apart. So as to planarize the surface and to remove dissimilarities in the substrate interactions, the substrate was then coated with ~2000 Å Accuglass 103AS Spin On Glass (Allied Signal). This produced a silicon oxide surface with slow undulations and a total peak−valley distance of 100−150 Å over the 4 μm array period, as measured by AFM and profilometry (Tencor Alpha Step). A schematic diagram of the substrate is shown in Figure 1. The opaque (<2% transmission) lines, separated by equally wide transparent spaces,

---

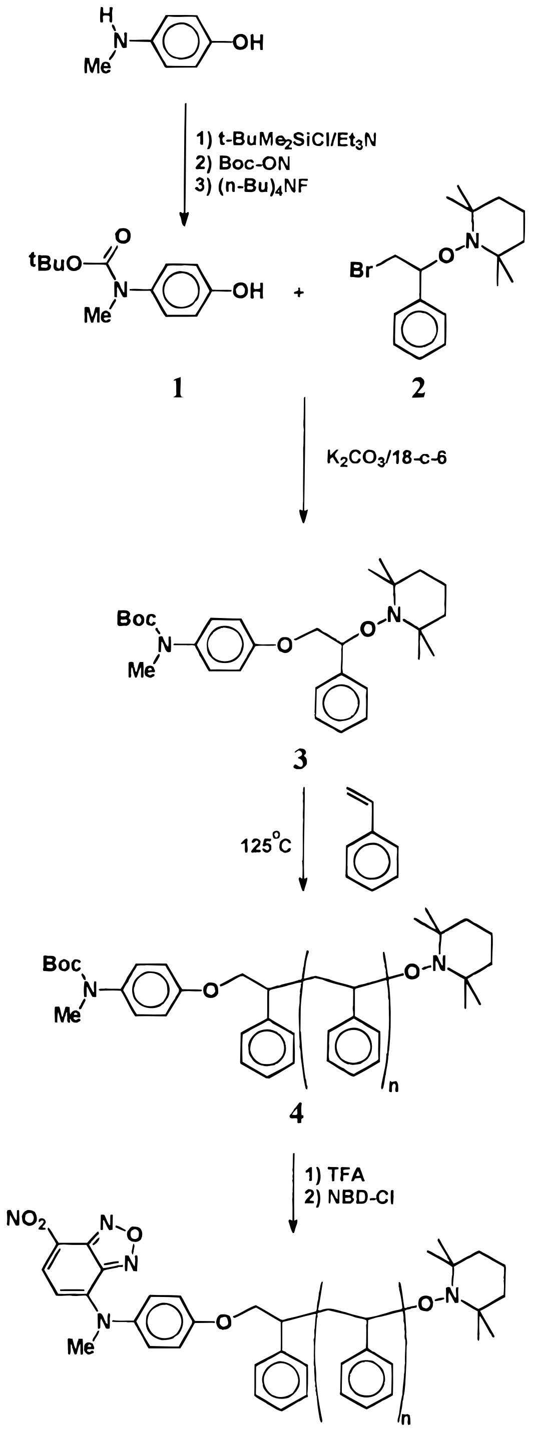
† Current address: Polymer Science and Engineering Dept., University of Massachusetts, Amherst, MA.

‡ Current address: University of Wollongong, Australia.

⊗ Abstract published in *Advance ACS Abstracts,* August 15, 1996.

S0024-9297(96)00749-8 CCC: $12.00

Scheme 1



created a square-wave pattern on the polymer sample when the system was illuminated.

Polymer films were spun from solution directly onto the sample gratings. This avoided the problem of motion of the pattern relative to the film during the course of the long-time experiment.[15] Film thicknesses were measured on films spun onto silicon wafers under the same conditions. By measuring many silicon wafers prepared in this manner, sample-to-sample variations in thickness of identically prepared samples were found to be under 3%. All films were annealed under vacuum at 140−170 °C for at least an hour to remove the solvent and allow the film to equilbrate.[11]

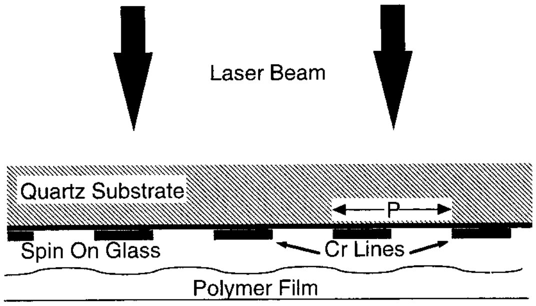


Figure 1. Diagram of a polymer film on mask of chrome lines. The pattern period P is 4 μm, the lines are 750 Å high, and the spin glass layer is ~2000 Å thick.

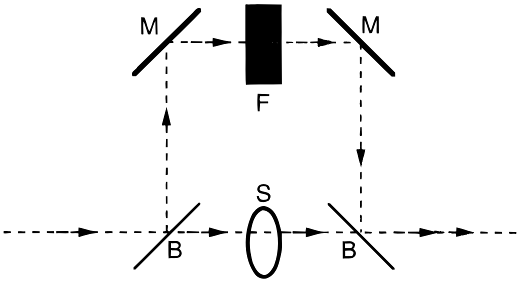


Figure 2. Array of beam splitters (B) and mirrors (M) directs and divides the output from an argon ion laser. One of the resulting beams, attenuated by neutral density filters (F), serves as the observation beam. The other is blocked by an electronic shutter (S) and is used to bleach the sample. The beams are then recombined so as to be collinear. The observation beam is 4 orders of magnitude less intense than the bleaching beam.

FRAPP Technique. The light source for our FRAPP experiments was a Coherent Innova 300 argon ion laser with an output of up to 1.5 W at 488 nm. An assembly of beam splitters, filters, and shutters (Figure 2) produced collinear high- and low-power beams for bleaching and observation. In general, the laser was operated at 400 mW for fluorescence observation and 1 W for bleaching purposes, resulting in a light intensity at the sample surface of ~36 μW and ~350 mW, respectively. A mechanical chopper was included in the light path, limiting sample illumination to 3 s/min. Measurements of a static, unbleached sample for over 12 h indicate that extended illumination with the observation beam does not measurably bleach the sample.

The laser was focused onto the sample using a Leitz fluorescence microscope with an Olympus 20× objective. The sample was held fixed in the field of view using a Mettler FP82 hot stage and equilibrated at 140 °C. The hot stage limited the area on the sample over which an individual measurement was made to a circle with a ~2 mm diameter. Thus, diffusion in the area between ~500 lines was observed, minimizing the effect of small defects in any one line.

Fluorescence from the sample was collected by the microscope optics, filtered to remove light at the excitation wavelength, and focused onto the photocathode of an RCA C31034-A photomultiplier tube. A Princeton Applied Research photon-counting system (Models 1112 and 1121) was used to measure the fluorescence intensity. The photon count rate of 10^4-10^5 was 2−3 orders of magnitude above the background. An HP7133A chart recorder was used to accumulate the data over the extended periods (2−10 h) of the experiments.

The FRAPP technique follows the diffusion of fluorescently tagged polymers spread uniformly throughout a polymer matrix. In our experiments, the samples were bleached with a striped pattern to yield alternating bands of high and low fluorescence (Figure 3). Integrating the intensity from the periodic dependence of the resulting fluorophore distribution leads to a simple solution of the diffusion equation:[15]

$$I = A + Be^{-t/\tau} \tag{1}$$

The time constant τ depends directly on the square of the pattern period,P, and inversely on the diffusion coefficient, D:

$$\tau = P^2/4\pi^2D \tag{2}$$

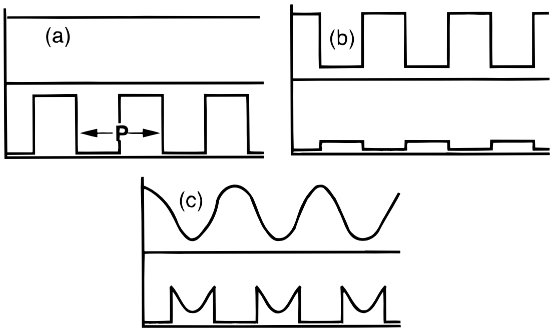


Figure 3. Schematic of chromophore distribution (upper line) and observed intensity pattern (lower line) in a polymer film. The chrome lines on the substrate block the beam, and no fluorescence is observed from those areas. The pattern period P is 4 μm. Three different times are presented: (a) before bleaching; (b) immediately following bleaching; (c) after some diffusion has occurred.

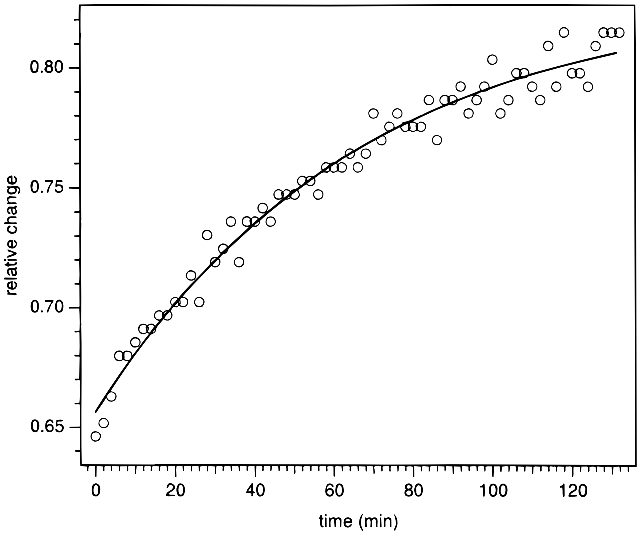


Figure 4. Graph of fluorescence intensity vs time for photobleaching recovery. The substrate was bleached to 64% of the initial intensity and recovered to 81% of the initial intensity. The solid line is the best fit to a single exponential.

Thus, by knowing the period and measuring the time constant, the diffusion coefficient can be easily calculated. Further details and the general theory behind FRAPP are described in extensive detail elsewhere.[14−18,21−23]

Results

Figure 4 is a graph of fluorescence intensity vs time for a 3360 Å thick film of PS, where 37% of the molecules have been tagged. The points are the experimental data, and the solid line is a best fit single exponential recovery curve to the data (eq 1). As can be seen, a single exponential describes the recovery well. Calculated deviations are evenly distributed about zero. The time constant for this fit is 4000 ± 300 s which, from eq 2 and the 4 μm bleach pattern period, yields a diffusion coefficient of $(10.1 \pm 0.8) \times 10^{-13}$ cm^2/s.

Shown in Figure 5 is the diffusion coefficient as a function of the film thickness from ~500−4500 Å. The error bars are indicative of the quality and reproducibility of the fit to each individual data set. Measurements at 4500 Å were taken from three spots on two different samples, while measurements at 3360 and 1880 Å were taken from two spots on the same sample. Thus, these measurements attest to the reproducibility of our technique. Each data point results from a fit to data over 2−5 time constants.

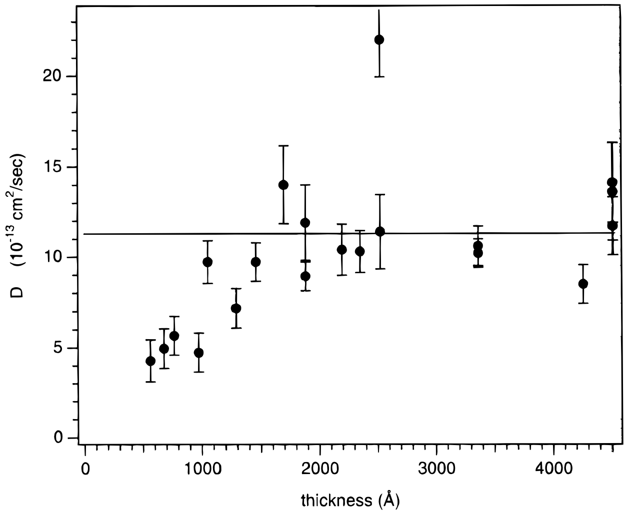


Figure 5. Diffusion coefficient as a function of film thickness. The solid line represents the average of the diffusion coefficient measured in the thick film regime. Film thickness variations are under 30%.

Discussion

As can be seen in Figure 5, the diffusion coefficient as a function of the film thickness for films greater than 500 Å falls into two regimes. If the film thickness is greater than 1500 Å the diffusion coefficient is independent of the film thickness with an average value of 11.2×10^{-13} cm^2/s. This is in agreement with the range of diffusion coefficients measured by Antonietti et al.[17,18] and Green et al.[4] for bulk polystyrene. As the film thickness decreases below ~1500 Å, the diffusion coefficient decreases. In fact, for a polystyrene film with a thickness of 500 Å, the diffusion coefficient is reduced by over a factor of 2. Our measurements did not permit the investigation of thinner films due to decreasing signal-to-noise ratio. Consequently, it is now known if a limiting value of the diffusion coefficient has been reached or whether the diffusion coefficient would decrease further.

It is difficult to argue that the reduction in the diffusion coefficient or the mobility of the polymer chain results for finite size or confinement effects. For the polymer under investigation here, the radius of gyration is ~30 Å. Thus, the thickness where perturbations to the mobility are first seen correspond to a film that is on the order of 25 molecular diameters thick. At such a film thickness, the polymer chains can easily assume undistorted and unperturbed configurations. In fact, from simulations it has been shown that within a few segmental diameters from the surface the influence of the surface is minimal.[24−26] The chains should assume a normal random coil configuration. There is no question that, as the film thickness approaches molecular dimensions, a dramatic change in the mobility should be expected; however, this cannot be the origin of the reduction in the diffusion coefficient observed here.

In the vicinity of an interface, the dynamics of a polymer chain may be altered. In these studies there are two interfaces, the free surface and the polymer/substrate interface, which approach one another as the film thickness is decreased. The extent to which these interfaces perturb the dynamics depends on the strengths of the interactions between the polymer and the interfaces. At a free surface, there is preferential segregation of chain ends.[27,28] The presence of chain ends at the free surface will increase the free volume at the surface, and consequently enhance the mobility of the polymer.

In the case of polystyrene, ellipsometric studies by Keddie et al.[8] on thin films suggest that there is a marked enhancement in the mobility of chains at the free surface. Orts et al.[29] found that at temperatures well below the bulk T_g, a marked decrease of the film thickness occurred. Recently, Kajiyama and co-workers,[12] using atomic force microscopy, found that for polystyrene with molecular weights greater than 2×10^4, there was no evidence for a surface T_g lower than the bulk T_g; however, for lower molecular weights, a marked reduction in the T_g was evident. These results are in agreement with surface relaxation results of Liu et al.[30] where complete surface relaxation did not occur until the bulk T_g was reached. Each of these studies, which deal specifically with the dynamics of the free surface of a polymer film, indicate that the dynamics of the chains at the free surface either are not perturbed by the presence of the interface or are enhanced. These results would suggest that the diffusion constant in the vicinity of the free surface would either remain unchanged or increase and, consequently, cannot give rise to the effect observed here.

The substrate on which the polymer films are placed is a spin-on glass which is a polar surface. Reiter[31] and others[32] have shown, that depending on the molecular weight, film thickness, and temperature, polystyrene can dewet from such surfaces. Consequently, it would not be expected that the interactions between polystyrene and the substrate would be favorable. Results similar to that found here have been recently reported by Sokolov and co-workers.[13] Using forward recoil spectroscopy, these authors found that the diffusion coefficient depended upon their distance from the solid surface. As in our studies, they found that the diffusion coefficient of polystyrene was suppressed near a silicon oxide surface and that this persisted out to distances comparable to those reported here. They interpreted these results in terms of chains being pinned at the silicon oxide substrate, entrapping chain entanglements near the surface, since the substrate is immobile and there may be numerous contacts per chain between the substrate and the polymer. Such fixed contacts would severely retard the motion of the chains at the substrate. While this explanation accounts for the behavior observed by Sokolov et al. and the results reported here, it is difficult to justify this argument based on the strength of the interactions between the polymer and the substrate and the distance over which the effects propagate.

While we cannot provide a better explanation for the observed behavior than that put forth by Sokolov and co-workers,[13] there is another length scale that has not been considered up to this point. It is intersting to note that the fully extended chain length of the polystyrene chain of molecular weight 3×10^4 is ~1200 Å. This corresponds to the distance where the diffusion coefficient is found to decrease. For films of this thickness and less, the configurational space available to the molecules is reduced. However, the number of molecules that assume such a fully extended conformation will be vanishingly small. It is unclear, though, what role the contour length of the chain may play in affecting the mobility of the polymer in an entangled network. Whether the contour length is a critical parameter or not requires more extensive studies as a function of the molecular weight of the polymer.

In conclusion, we have shown that the mobility of polymer films is perturbed as the film is thinned. The diffusion coefficient decreases by more than a factor of 2 when the film thickness is less than ~1500 Å. This length scale far exceeds the length scales of the radius of gyration or the entanglement length of the polymer. The origin for the decreased mobility lays elsewhere and may be associated with the contour length of the polymer.

Acknowledgment. We wish to acknowledge the contributions of Drs. H. Ito and G. Wallraff for assistance with the lithography and Dr. B. Smith, M. Jurich, and J. Salem for technical assistance. This work was funded as part of the Center on Polymer Interfaces and Macromolecular Assemblies, NSF Grant DMR-9400354.

References and Notes

(1) Liu, F. P.; Gardner, D. J.; Wolcot, M. P. *Langmuir*, **1995**, *11*, 2675 and references therein.
(2) Brown, H. R.; Char, K.; Deline, V. R.; Green, P. F. *Macromolecules* **1993**, *26*, 4155.
(3) Russell, T. P. On the Reflectivity of Polymers: Neutrons and X-rays. *Physica B* **1996**, *221*, 267.
(4) Green, P. F.; Palmstrøm, C. J.; Mayer, J. W.; Kramer, E. J. *Macromolecules* **1985**, *18*, 501.
(5) Klein, J. *Science* **1990**, *250*, 640.
(6) Wallace, W. E.; Van Zanten, J. H.; Wu, W. L. *Phys. Rev. E* **1995**, *52*, R3329.
(7) Toney, M. F.; Russell, T. P.; Logan, J. A.; Kikuchi, H.; Sands, J. M.; Kumar, S. K. *Nature* **1995**, *374*, 709.
(8) Keddie, J. L.; Jones, R. A. L.; Cory, R. A. *Europhys. Lett.* **1994**, *27*, 59.
(9) Granik, S. *MRS Bull.* **1996**, *21*, 33.
(10) Hu, H. W.; Granik, S. *Science* **1992**, *258*, 1339.
(11) Reiter, G. *Europhys. Lett.* **1993**, *23*, 579 and references therein.
(12) Tanaka, K.; Taura, A.; Ge, S.; Takahara, A.; Kajiyama, T. *Macromolecules* **1996**, *29*, 3040.
(13) Zheng, X.; Sauer, B. B.; Van Alsten, J. G.; Schwartz, S. A.; Rafailovich, M. H.; Sokolov, J.; Rubinstein, M. *Phys. Rev. Lett.* **1995**, *74*, 407.
(14) Smith, B. A. In *Photophysical and Photochemical Tools in Polymer Science*; Winnik, M. A., Eds.; D. Reidel Publishing: 1986; pp 397−406 and references therein.
(15) Smith, B. A. *Macromolecules* **1982**, *15*, 469.
(16) Smith, B. A.; Mumby, S. J.; Samulski, E. T.; Yu, L. P. *Macromolecules* **1986**, *19*, 470.
(17) Antonietti, M.; Coutandin, J.; Grutter, R.; Sillescu, H. *Macromolecules* **1984**, *17*, 798.
(18) Antonietti, M.; Coutandin, J.; Sillescu, H. *Makromol. Chem., Rapid. Commun.* **1984**, *5*, 525.
(19) Hawker, C. J. *J. Am. Chem. Soc.* **1994**, *116*, 11314.
(20) Hawker, C. J.; Hedrick, J. L. *Macromolecules* **1995**, *28*, 2993.
(21) Santore, M. M.; Rebar, V. A. *Mater. Res. Soc. Symp. Proc.* **1995**, *366*, 421.
(22) Cicerone, M. T.; Blackburn, F. R.; Ediger, M. D. *Macromolecules* **1995**, *28*, 8224.
(23) Tilton, R. D.; Robertson, C. R.; Gast, A. P. *J. Colloid Interface Sci.* **1990**, *137*, 194.
(24) Theodorou, D. N. *Macromolecules* **1988**, *21*, 1391.
(25) Kumar, S. K.; Vacalello, M.; Yuon, D. Y. *Macromolecules* **1990**, *23*, 2189.
(26) Bitsanis, I.; Hadziioannou, G. *J. Chem. Phys.* **1990**, *92*, 3827.
(27) Zhao, W.; Zhao, X.; Rafailovich, M. H.; Sokolov, J.; Komposto, R. J.; Smith, J. J.; Dozier, W. D.; Mansfield, J.; Russell, T. P. *Macromolecules* **1993**, *26*, 561.
(28) Mayes, A. M. *Macromolecules* **1994**, *27*, 3114.
(29) Orts, W. J.; van Zanten, J. H.; Wu, W.; Satijia, S. K. *Phys. Rev. Lett.* **1993**, *71*, 867.
(30) Liu, Y.; Russell, T. P.; Brown, H. R.; Sumant, M.; Stöhr, J., submitted to *Nature*.
(31) Reiter, G. *Phys. Rev. Lett.* **1992**, *68*, 75.
(32) Zhao, W.; Rafailovich, M. H.; Sokolov, J.; Fetters, L. J.; Plano, R.; Sanyal, M. K.; Sinha, S. K.; Sauer, B. B. Phys. *Rev. Lett.* **1993**, *70*, 1453.

MA960749N