Macromolecules **2007,** *40,* 3819−3830

Ultralow Interfacial Tensions of Polymer/Polymer Interfaces with Diblock Copolymer Surfactants

Kwanho Chang, Christopher W. Macosko, and David C. Morse*

Department of Chemical Engineering and Materials Science, University of Minnesota, Minneapolis, Minnesota 55455

Received October 2, 2006; Revised Manuscript Received January 23, 2007

ABSTRACT: The interfacial tension γ between polyisoprene (PI) and polydimethylsiloxane (PDMS) homopolymers mixed with poly(isoprene-*b*-dimethylsiloxane) (IDMS) diblock copolymers has been measured with a spinning drop tensiometer. Measurements have been conducted for mixtures containing each of 12 copolymers, in which the PDMS volume fraction f_{DMS} varies from 0.49 to 0.73, and for mixtures containing a symmetric copolymer and PI homopolymers of varying molecular weight. The measured interfacial tension is found to be independent of copolymer concentration above an apparent critical concentration of order 0.1 wt % copolymer. Mixtures with a nearly symmetric copolymer are found to exhibit ultralow interfacial tensions, up to 3 orders of magnitude less than that of the bare PI/PDMS interface. Results are compared to the predictions of a numerical self-consistent field theory for the interfacial tension of an interface between a PDMS phase containing swollen spherical micelles and a phase of nearly pure PI. Agreement between theory and experiment is excellent for sufficiently asymmetric copolymers, with $f_{\mathrm{DMS}} > 0.63$. Measured values of γ are significantly lower than predictions for $0.5 < f_{\mathrm{DMS}} < 0.6$, however, and depend very sensitively upon f_{DMS} over a narrow range $0.60 \leq f_{\mathrm{DMS}} \leq 0.63$. Kinetic limitations that may be relevant to these experiments are also analyzed and discussed.

1. Introduction

When small amounts of surfactant are added to a mixture of oil and water, the oil−water interfacial tension initially decreases with increasing concentration of dissolved surfactant, while the amount of adsorbed surfactant increases. Both the interfacial tension and the interfacial coverage generally saturate, however, when the surfactant concentration exceeds a critical value, above which additional surfactant begins to aggregate into micelles in either oil or water, or to segregate into a third surfactant rich phase.[1] This saturation of macroscopic interfacial tension above an apparent critical micelle concentration (cmc) is observed independent of the form of the resulting surfactant aggregates: It occurs whether surfactant aggregates into swollen spherical micelles, or into monolayers, within a bicontinuous microemulsion. The saturation value of the macroscopic interfacial tension is, however, very sensitive to the free energy per surfactant molecule within the coexisting micellar or microemulsion structure.

Extremely low interfacial tensions can be obtained in systems of "balanced" surfactants, for which the thermodynamically preferred form of aggregation is a surfactant monolayer with no spontaneous curvature (i.e., a vanishing preferred value for the mean curvature). Systems of such balanced surfactants generally form either a bicontinuous microemulsion or a lamellar phase. Either of these structures may exhibit two and three phase coexistence with phases of excess oil and/or water. In some mixtures of oil, water, and nonionic alkyl−poly(ethylene oxide) surfactants,[2−5] the monolayer spontaneous curvature is a sensitive function of temperature T. In these systems, the macroscopic interfacial tension $\gamma(T)$ between oil and water phases reaches a minimum at a "balance" temperature T_{b} at which the spontaneous curvature passes through zero. The minimum interfacial tension can be several orders of magnitude less than the bare oil−water interfacial tension.

In mixtures of immiscible A and B homopolymers with small amounts of AB diblock copolymer, the copolymer plays a role analogous to that of small molecule surfactant in oil−water mixtures. Bicontinuous microemulsions have been observed in ternary polymer mixtures, both in symmetric A/B/AB mixtures,[6−8] and in A/B/AC mixtures in which the AC copolymer and temperature have been chosen so as to obtain a balanced surfactant.[9,10] The observation of a bicontinuous phase indirectly suggests that a state of very low interfacial tension can be achieved in such mixtures.

Direct measurements of the macroscopic interfacial tension between polymer liquids in the presence of copolymer additives[11−16] have, however, thus far not yielded ultralow interfacial tensions comparable to those measured in balanced small molecule mixtures. The largest previously reported reduction in γ due to a diblock copolymer additive appears to be a decrease by less than 1 order of magnitude, to 18% of the interfacial tension of the bare interface.[12] Other measurements have often yielded interfacial tension decreases of less than 50% in systems of nearly symmetric diblocks,[11,14,15] for which equilibrium theory would predict much more dramatic decreases.

Here, we report interfacial tension measurements for systems of polyisoprene (PI) and polydimethylsiloxane (PDMS) homopolymers with poly(isoprene-*b*-dimethylsiloxane) (IDMS) diblock copolymer surfactants. In such systems, the monolayer spontaneous curvature cannot be easily controlled by varying the temperature. To systematically vary the spontaneous curvature, we have instead conducted experiments at fixed temperature for mixtures in which, in one sequence, we vary the molecular weight of the PDMS block of the copolymer, and, in two other sequences, we vary the molecular weight of the PI homopolymer in the presence of a symmetric copolymer.

One advantage of the study of block copolymers as model surfactants is the ability of numerical self-consistent field theory (SCFT) to provide rather accurate predictions of free energies for polymeric monolayers and micelles. We have recently used SCFT to predict the equilibrium interfacial tension between a phase of nearly pure B homopolymer and a coexisting phase of A homopolymer that contains spherical micelles of AB

10.1021/ma062277a CCC: $37.00

diblock copolymer.[17] This model allows the micelles (or microemulsion droplets) to swell by emulsifying the B homopolymer within the micelle core. For mixtures of symmetric homopolymers with equal degrees of polymerization, and monomers with equal statistical segment lengths, this model predicts that γ should extrapolate to zero in the limit of a symmetric copolymer, with $f_A = 1/2$, and vary quadratically with f_A around this minimum. Analogies to experimental results obtained with mixtures of oil, water, and non-ionic surfactant, which form a bicontinuous (rather than droplet) microemulsion near the balance point, suggest that γ may instead reach a very small but nonzero minimum value at the balance point.[26] One goal of the present study is to quantitatively test these SCFT predictions.

The most important differences between small-molecule and macromolecule surfactants are differences in the rates of equilibration, rather than any difference in equilibrium behavior. The low diffusivity of a polymeric surfactant in a polymeric matrix makes it difficult to guarantee that a state of macroscopic phase equilibrium will be reached within the types of apparatus that are used to measure interfacial tension. In both the pendent drop method[11−13] and the spinning drop method used here,[19−21] the tension of an interface between a macroscopic (e.g., millimeter) drop of one liquid and a surrounding matrix of another is inferred from the deformation of the drop, which is caused by gravitational forces acting on a pendent drop or centrifugal forces acting on a spinning drop. To guarantee *a priori* that such a sample would reach a state of global thermodynamic equilibrium, with a copolymer that is slightly soluble in both phases, it would be necessary to allow time for copolymer to diffuse across the entire macroscopic drop and matrix and thereby to establish a homogeneous copolymer chemical potential throughout the sample. In polymer mixtures, this criterion generally leads to prohibitively long times, even for the relatively low molecular weight polymers used in these and previous interfacial tension measurements.

Careful measurements of interfacial tension in mixtures of oil, water, and small molecule surfactants have been carried out by first allowing a mixture to undergo spontaneous macroscopic phase separation[5] and then preparing samples for interfacial tension measurements by injecting a drop of material taken from one of two coexisting phases into a matrix of material taken from the other. We have tried to imitate this procedure, but we failed to obtain true macroscopic phase separation (i.e., a sample with two optically clear phases and a distinct meniscus) even with the help of centrifugation.

The measurements presented here, like most previous measurements with ternary polymer mixtures, have instead been carried out by initially mixing the copolymer into only one of the two phases. We premix the copolymer with a matrix of the PDMS homopolymer and then inject into this a drop of pure PI. Several researchers have previously noted that the slow diffusion of copolymer appears to strongly affect the results of interfacial tension measurements in such samples.[12,15,16] Specifically, it has been observed that significantly different results can be obtained in the pendent drop experiments depending upon whether the copolymer is initially premixed with the drop or the matrix material. As a result, it has remained difficult to obtain reliable measurements of *equilibrium* interfacial tensions in mixtures containing copolymer additives.

Table 1. Material Characteristics of Homopolymers

sample code	M_n (g/mol)[a]	M_w/M_n	N[b]	η_o (Pa·s)[c]	γ_o (mN/m)[d]
PI1	2900	1.08	42	1.3	2.6
PI2	4600	1.07	68	3.0	3.1
PI3	6000	1.09	88	4.1	
PI4	6600	1.06	97	7.2	3.4
PI5	7700	1.08	113	8.9	3.4
PI6	9600	1.06	141	11.7	3.5
PI7	15800	1.06	231	47.0	3.6
PDMS1	6200	1.08	84	0.1	
PDMS2	8000	1.10	107		

[a] The number-average molecular weights determined by GPC and converted using polystyrene standards. [b] On the basis of a reference volume $\upsilon = 126.1$ Å. [c] Zero shear viscosity measured with parallel plate rheometry at 298 K. [d] Bare interfacial tension with PDMS1.

Recently, one of us (Morse) analyzed a transport problem relevant to this experiment, in which copolymer is initially mixed into the matrix phase with a concentration greater than the critical micelle concentration (cmc) and then diffuses to the interface and (to some extent) into a drop of initially pure homopolymer.[22] The analysis showed that, if the copolymer has a comparable solubility in both phases (as expected for a nearly symmetric diblock), it is possible for the interface to reach a quasi-steady nonequilibrium state in which the interfacial coverage is depleted below its equilibrium value by a continual diffusion of copolymer into the drop. This analysis suggested that the optimal system for measuring the equilibrium interfacial tension in the presence of a nearly symmetric diblock copolymer would be one in which the copolymer tracer diffusivity is much higher in the phase to which the copolymer is initially added than in the other phase. For the work reported here, we have thus chosen a model system of low molecular weight liquid polymers in which the copolymer tracer diffusivity is relatively high in both phases but is expected to be significantly higher in the PDMS matrix than in the more viscous PI drop.

2. Experiment

2.1. Materials. All polymers used in this study were synthesized by anionic polymerization.[23] To synthesize PI homopolymers, isoprene (Aldrich) monomers were first stirred with calcium hydride (CaH_2) overnight and purified with *n*-butyl lithium twice under vacuum for 2 h each. Polymerization was initiated with *sec*-butyl lithium in 10 vol % cyclohexane solution and carried out at 40 °C for 6 h. The resulting solution of PI homopolymer was terminated using acidic methanol, washed several times with deionized water, and finally dried in a vacuum oven until the weight remained constant.

To synthesize PDMS homopolymers, hexamethylcyclotrisiloxane (D_3, Aldrich) was stirred over calcium hydride at 80−90 °C for 4 h and further purified with dibutylmagnesium under vacuum for 1.5 h.[24] After initiation with *sec*-butyl lithium, at least 18 h was required to ensure the complete activation of D_3 in 10 vol % cyclohexane at room temperature. Actual polymerization started upon subsequent addition of an equal volume of tetrahydrofuran (THF). After 2−3 h, the reaction was terminated with a 10-fold molar excess of chlorotrimethylsilane (Aldrich) achieving the total conversion of 40−45%. The final solution was redissolved in cyclohexane after the majority of THF was removed by rotary evaporation. It was immediately washed with 5−10 wt % sodium bicarbonate ($NaHCO_3$) aqueous solution, and subsequently with deionized water. The products were filtered with 0.2 μm pore filter disks and further dried in a vacuum oven for 2−3 weeks in order to remove residual solvent and unreacted D_3 monomer. The molecular characteristics of homopolymers are listed in Table 1.

Poly(isoprene-*b*-dimethylsiloxane) (IDMS)[24] block copolymers were polymerized by the sequential addition of isoprene and D_3 monomers in the manner described above for homopolymers, except that the IDMS solution was precipitated in a 3:1 vol/vol mixture of methanol and 2-propanol. Before adding D_3 monomers for the second block, an aliquot of PI block was removed and quenched in methanol for analysis. The molecular characteristics of that block are summarized in Table 2. Sometimes, a small amount of the IDMS

Table 2. Material Characteristics of Block Copolymers

sample code	M_{PI} (g/mol)[a]	M_w/M_n	f_A[b]	γ(0.1%)[c]	γ(0.2%)	γ(0.3%)	γ(0.4%)
IDMS1	4800	1.06	0.49	0.0011	0.0014	0.0013	
IDMS2	4400	1.15	0.50		0.0031		
IDMS3	4000	1.08	0.50	0.0007			
IDMS4	4800	1.09	0.53		0.0060		
IDMS5	4800	1.11	0.57		0.0094		
IDMS6	4900	1.07	0.58	0.0084			
IDMS7	4900	1.09	0.60	0.050	0.016	0.020	
IDMS8	5200	1.09	0.61	0.12		0.064	
IDMS9	4400	1.13	0.63		0.17		0.064
IDMS10	4400	1.13	0.66	0.26	0.25		0.22
IDMS11	4700	1.05	0.71		0.435		0.43
IDMS12	4700	1.04	0.73		0.50		0.49
IDMS13	9300	1.07	0.50				

[a] The number-average molecular weights of PI blocks determined by GPC based on polystyrene standards and converted using a universal calibration. [b] The volume fraction of PDMS within IDMS. [c] Interfacial tension (mN/m) in the system of PI4/PDMS1/IDMS.

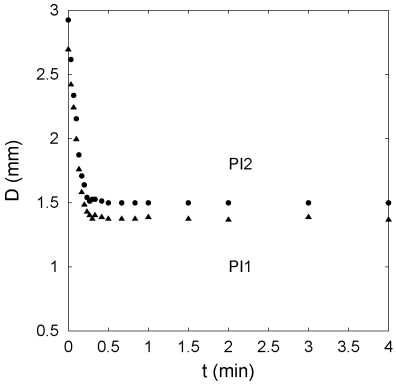

Figure 1. Diameter of PI1 and PI2 drops in a PDMS1 matrix as a function of time, following a sudden increase in the rate of rotation (spin-up) to 6300 rpm, in the absence of copolymer additive.

solution was cannulated out during the synthesis of the DMS block and terminated in a separate preflamed flask whereas the solution in a main reactor was terminated later. The IDMS pairs made in this way are IDMS2/IDMS9, IDMS4/IDMS5, IDMS6/IDMS7, and IDMS11/IDMS12. A small amount of PDMS homopolymer might be produced during the polymerization of IDMS,[24] but a distinct peak of the PDMS homopolymer was not identified in gel permeation chromatography (GPC) data. Such a small homopolymer peak could be hidden in the tail of the IDMS peak due to similar hydrodynamic volumes, but no further fractionation was conducted.

The number (M_n) and weight (M_w) averaged molecular weights of PI were determined with GPC (in THF) using polystyrene standards and a universal calibration curve. Those of PDMS and IDMS were determined with GPC (in toluene) using both refractive index and light scattering detectors. NMR was used to calculate the block ratio $f_A = N_{CA}/N_C$ of IDMS, where N_{CA} is a length of PDMS block and N_C is a total length of IDMS. Here and hereafter, the subscript A denotes PDMS, B denotes PI, and C is used to denote a property of the copolymer. Also, NMR was used to obtain 1,4 fractions of PI homopolymer and blocks, which were all at least 94%, and to confirm M_n of the PDMS homopolymers.

The zero shear viscosity η_o of each homopolymer was measured with a TA Instruments ARES rheometer using a dynamic rate sweep mode at room temperature with 25 mm parallel plates, a 1 mm gap, and 10% strain. The results are reported in Table 1.

The PDMS matrix materials used in our interfacial tension measurements were prepared by premixing IDMS block copolymers with pure PDMS homopolymer at room temperature, at concentrations of 0.1−0.4 wt %, which are all above the cmc (Figure 4). A total volume of 1 mL was prepared for each sample and kept in a vacuum oven until the mixtures appeared homogeneous. This usually took 4−5 h at room temperature without mechanical stirring.

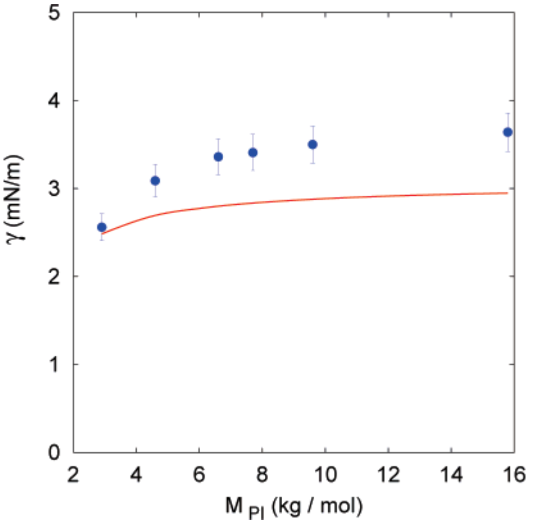

Figure 2. Bare interfacial tension between PI and PDMS1 in the absence of block copolymer as a function of molecular weights of PI. The solid line is the SCFT prediction using $\chi = 0.175$.

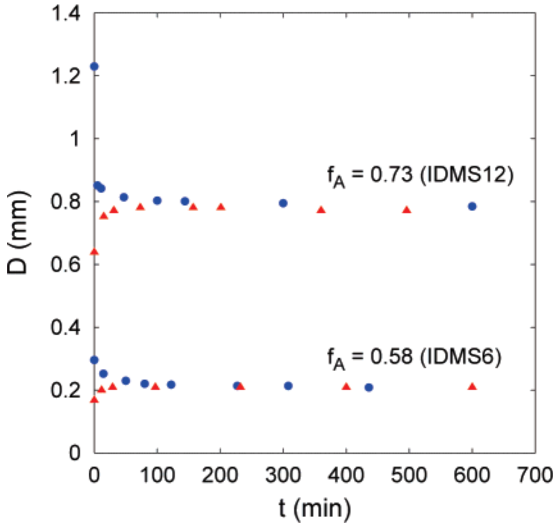

Figure 3. Drop diameter vs time for drops of PI4 in PDMS1 premixed with an IDMS6 copolymer ($f_A = 0.58$), and PI4 in PDMS2 premixed with an asymmetric IDMS12 copolymer ($f_A = 0.73$) in both spin up (circles) and spin down (triangles) experiments. The concentrations of IDMS6 and IDMS12 in the corresponding PDMS matrices are 0.1 and 0.2 wt %, respectively. The final rotation frequency is 6300 rpm in all of the measurements shown.

2.2. Interfacial Tension Measurement. Interfacial tension was measured with a spinning drop tensiometer (SDT) in the laboratory of Prof. Daniel Joseph. In this instrument,[20,21] an electric motor rotates a horizontal glass tube containing a liquid drop of a less dense phase (PI) in a denser matrix (PDMS) at a constant angular velocity.

For each sample, the PDMS matrix (density $\rho_A = 0.970$ g/mol)[25] was poured into a glass tube with a 6 mm inner diameter, which is 15 cm long. One end of the glass tube in the SDT is sealed by a plug equipped with a set of terraced calibration posts. These posts are used to calibrate observations of the drop diameter through a microscope. Calibration is necessary to correct optical distortion caused by the curved wall of the tube. We used either of two different plugs for which the terrace diameters range from 0.3 to 0.5 mm or from 0.5 to 2 mm, respectively, depending on the expected final diameter of the drop. The glass tube was placed in vacuum until no air bubbles came out of the gap between the O-rings around the plug and the glass wall. Then, a pure PI drop ($\rho_B = 0.900$ g/mol),[25] with an initial diameter of 0.5−2 mm chosen so as to give convenient final dimensions, was injected into the

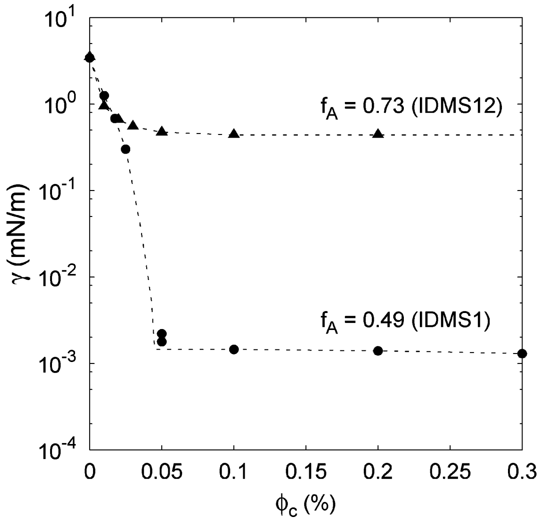

Figure 4. Interfacial tension reduction of PI4/PDMS1 and PI4/PDMS2 as a function of the concentration of IDMS1 and IDMS12, respectively. The dashed lines are guides to the eye.

middle of the PDMS matrix using a glass pipet. Another plug with a threaded hole at the center was then quickly pushed into the glass tube, until the first drop of the PDMS matrix was pushed out through the hole in the plug. The hole was then tightly sealed with a bolt and an O-ring before the PI drop could rise significantly, and the glass tube was loaded into the SDT.

In an attempt to reduce the effects of the slow diffusion of block copolymer into the drop, many of our interfacial tension measurements were carried out on samples that were stored for 1−4 weeks after injection of the pure PI drop into a PDMS/copolymer matrix. This treatment did not appear to have any effect upon the results.

Centrifugal forces deform the drop into a shape that, when the deformation is large, is well approximated as a cylinder of length l and diameter d with hemispherical caps. When $l/d > 4$, the interfacial tension γ for such a drop is related to the drop diameter d, angular velocity ω [radians/time], and density difference $\Delta\rho$ by[19]

$$\gamma = \frac{1}{32}\Delta\rho\omega^2 d^3 \tag{1}$$

The density difference for the polymers studied here is $\Delta\rho = \rho_A - \rho_B = 0.070$ g/mol. In each measurement, the initial drop size and angular velocity were chosen for each sample so as to give $l/d \simeq 5$, while using rotation frequencies of 3000−6000 rpm.

The rotation of the sample was synchronized with the frequency of a stroboscope in order to obtain still images of the rotating drop with a video camera. Since γ is proportional to d^3, it was critical to get images of sharp drop edges. The stroboscope minimized the effect of off-centered movements of both the drop and the calibration posts.

During the measurements, both spin-up and spin-down experiments were carried out to confirm that the system had reached hydrodynamic equilibrium.[20,21] Also, a few samples were run at two different angular velocities to confirm that the same value of γ was obtained at different rotation rates. Individual measurements of γ were reproducible within ca. ±5%. This error is primarily due to the uncertainty in diameter measurement.

3. Results

3.1. Bare Interfacial Tension. The interfacial tension γ_o in the absence of copolymer has been measured for interfaces between PDMS1 and PI homopolymers PI1−PI7. In the absence of copolymer, the drop diameter typically relaxed to its final value with a characteristic time of order 10 s in both spin-up and spin-down experiments, as shown in Figure 1.

Table 1 and Figure 2 show the resulting values of γ_o as a function of PI molecular weight M_{PI}. The interfacial tension reaches an apparent plateau value of 3.6 mN/m for the highest PI molecular weights. This plateau value for γ_o is in a reasonable agreement with the literature value of 3.2 mN/m,[26] which was measured using a higher molecular weight commercial grade homopolymers, for which the reported density difference was $\Delta\rho = 0.064$ g/cm^3, vs 0.070 g/cm^3 for our samples.

The solid line in Figure 2 is a SCFT prediction for this series of samples. The SCFT calculations were similar to those discussed in ref 18. These calculations used values of $N_{PI} = 97$, $N_{PDMS} = 84$, $N_{IDMS} = 70(\mathrm{I}) - 67(\mathrm{DMS})$, based on a common reference volume $v = 126.1$ Å, a Flory−Huggins parameter $\chi = 0.175$, and statistical segment lengths of $b_{PDMS} = 5.57$ Å and $b_{PI} = 6.38$ Å. All other SCFT calculations in this paper use the same values of v, χ, and b. This value of χ was chosen to fit our measurements of the initial decrease in interfacial tension with small amounts of added copolymer and of the apparent cmc, which are discussed in the following subsection. Our chosen value of $\chi = 0.175$ is slightly larger than the value $\chi = 0.146$ at $T = 298$ K reported by Cochran *et al.*,[28] which was obtained by fitting T_{ODT} of two different symmetric PI-*b*-PDMS block copolymers with the equation $\chi(T) = A/T + B$ and assuming $(\chi N_C)_{ODT} = 10.495$.[29] SCFT predictions of the bare interfacial tension using $\chi = 0.175$ underestimate the interfacial tension at high PI molecular weights by about 10%. Use of the lower literature value would yield a slightly larger discrepancy.

3.2. Dependence on Copolymer Concentration. The interfacial tension in the presence of block copolymer has been measured for interfaces between PI4 and PDMS1 (or PDMS2) premixed with copolymers as a function of copolymer concentration.

The time required for the drop to reach its final diameter after a sudden change in the rotation rate of the spinning drop tensiometer is significantly longer in the presence of a block copolymer additive than in its absence. Figure 3 shows representative transient behaviors of the diameter of the PI4 drop during spin-up and spin-down experiments with 0.1 wt % of IDMS6 in PDMS1 and 0.2 wt % of IDMS12 in PDMS2, respectively. At concentrations above the cmc, most of the change in drop diameter typically occurs within 10−20 min in both spin up and spin down experiments. We did not, however, take measurements at sufficiently closely spaced intervals to accurately characterize the dynamics of drop equilibration in systems with added copolymer. Steady state measurements were taken after a constant rotation rate had been maintained for a waiting period of 24 h. This was found to be sufficient to obtain a time-independent value in all but a few samples (The exceptions are discussed below).

Figure 4 shows the dependence of the measured steady-state interfacial tension γ upon the concentration of copolymer added to the PDMS, for two different copolymers. Dashed lines are merely guides for the eye. When the highly asymmetric block copolymer IDMS12, with $f_A = 0.73$, was added to PI4/PDMS2, γ decreased to a minimum value of 0.44 mN/m. This is an 87% reduction relative to the bare interfacial tension, which is comparable to the maximum reduction found in previous studies.[12,13] However, when the symmetric block copolymer IDMS1 was added to PI4/PDMS1, γ dropped to a strikingly low interfacial tension of approximately 0.0015 mN/m at concentrations above an apparent cmc of less than 0.05% copolymer. This is a reduction in γ by more than 3 orders of magnitude. While similarly dramatic decreases have been observed in systems with balanced small molecule surfactants,

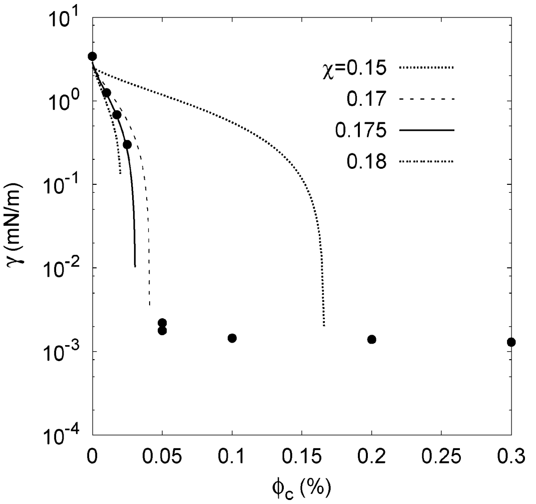

Figure 5. Interfacial tension reduction between PI4 and PDMS1 as a function of the concentration of IDMS1 added to the PDMS matrix. The lines are SCFT predictions with four different values of χ.

nothing comparable has previously been observed in a polymeric system.

Figure 5 compares our results for the system of PI4/PDMS1 and symmetric IDMS1 copolymer to SCFT predictions of equilibrium interfacial tension obtained with several slightly different values of χ. The SCFT calculations are similar to those presented in ref 17 and are based on a model of the PDMS phase as an equilibrium phase of swollen spherical micelles that coexists with a phase of nearly pure PI. Both the initial slope, $d\gamma/d\phi_c$ near $\phi_c = 0$, and the cmc are extremely sensitive to the chosen value of χ. This is because both quantities are known to vary with χ as $e^{-\chi N_C f_B}$, where $\chi N_C f_B \sim 12$ for this system. All other SCFT results presented in this paper use the value $\chi = 0.175$ chosen to fit this data for the concentration dependence of γ below the cmc.

3.3. Dependence on Copolymer Composition. We have measured interfacial tensions between a PI4 drop and a PDMS1 matrix premixed with each of the 12 copolymers IDMS1−IDMS12 listed in Table 2, at copolymer concentrations above the apparent cmc. These copolymers all have PI blocks of similar molecular weight, $M_{PI} \sim 5K$, but PDMS blocks of varying molecular weight. The volume fraction of PDMS in this series varies from 0.49 to 0.73. Measurements were taken with copolymer concentrations varying from 0.1 to 0.4 wt % in order to confirm that the interfacial tension is generally independent of concentration. Figure 6 shows the interfacial tension above the apparent cmc as a function of $f_A = f_{DMS}$. Figure 7 shows the same data on a logarithmic scale for interfacial tension. For most copolymers, values are shown for more than one concentration. It should be apparent that the values γ obtained at concentrations above the cmc are highly reproducible, but are not a smooth function of f_A. Starting from an interfacial tension of order 10^{-3} mN/m near the symmetric copolymer $f_A = 0.49$ (IDMS1), γ first increases relatively slowly with increasing f_A, reaching about 10^{-2} mN/m for $f_A = 0.58$ (IDMS6), but then changes by roughly an order of magnitude over a narrow range of $f_A = 0.60-0.63$ (IDMS7−IDMS9). For $f_A \geq 0.66$ (IDMS10−IDMS12), γ again appears to increase smoothly with increasing f_A. This seemingly discontinuous dependence on f_A is more obvious on the logarithmic scale used in Figure 7.

SCFT predictions of the values of γ above the cmc, hereafter denoted γ_{cmc}, are shown in Figure 6 in two different forms: The open circles are the results of three SCFT simulations similar to those presented in ref 17. In these calculations, the cmc was obtained from a series of SCFT simulations of swollen spherical micelles in the PDMS matrix, and γ_{cmc} was obtained from separate SCFT simulations of flat interface at the corresponding cmc. These simulations were carried out on three systems containing homopolymers with $N_A = 84$ and $N_B = 97$, corresponding to PDMS1 and PI4, and three copolymers with a common PI block length of $f_B N_C = 70$ and PDMS block lengths of $f_A N_C = 105$, 130, and 186.

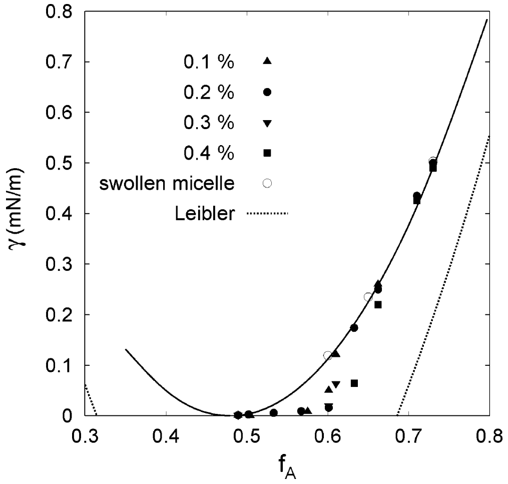

Figure 6. Interfacial tension in PI4/PDMS1/IDMS systems as a function of the block ratio f_A of IDMS, compared to SCFT predictions. Closed symbols are measurements of steady-state interfacial tensions with different copolymers from a series of IDMS1−IDMS12 at several concentrations. The open circles are the predictions of γ_{cmc} of three SCFT simulations of flat interfaces at the cmc of swollen micelles. The solid line is the prediction of eq 2. Leibler's theory[30] is shown as a dotted line.

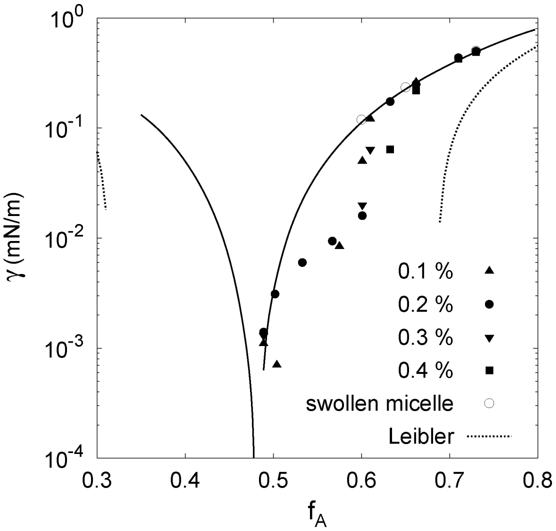

Figure 7. Experimental data and calculations of Figure 6 plotted on a logarithmic scale. Near the balance point, measured values are considerably lower than those predicted by SCFT.

The solid line in Figure 6 is the result of an approximation for γ_{cmc} that is based on the Helfrich theory of interfacial bending elasticity of weakly curved monolayers, as presented in ref 17. This approximation yields an interfacial tension that depends on f_A as

$$\gamma_{cmc} = \frac{\tau'^2}{2\kappa_+}(f_A - f_A^{bal})^2 \tag{2}$$

for a series of systems containing the same pair of homopolymers and copolymer with a fixed core block size $f_B N_C$. Here,

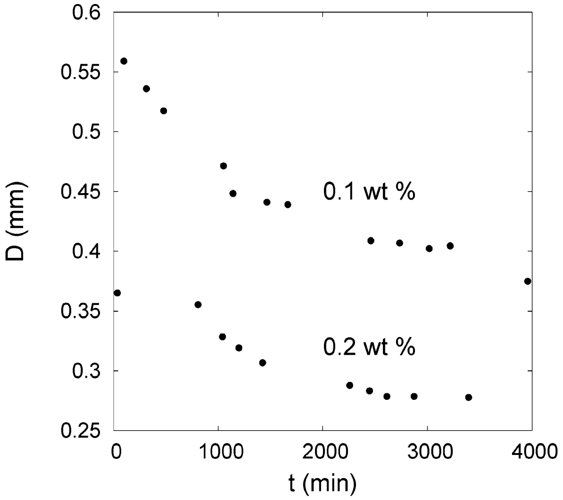

Figure 8. Time-dependent diameter of a PI4 drop in the PDMS1 matrix at a rotation frequency of 6300 rpm with two different concentrations of IDMS7 ($f_A = 0.60$), 0.1 and 0.2 wt %.

f_A^{bal} is the value of f_A at which a balanced saturated monolayer, with $\tau = 0$, is formed, $\kappa_+ = \kappa + \bar{\kappa}/2$ is the bending rigidity for a spherically curved surface (i.e., the second derivative of interfacial tension with respect to mean curvature $C = 2/R$ at fixed copolymer chemical potential), τ is the first derivative of interfacial tension with respect to mean curvature, evaluated at $C = 0$, and $\tau' = \partial\tau/\partial f_A$. In this approximation, κ_+ and τ' are evaluated at $f_A = f_A^{bal}$. The parameters f_A^{bal}, κ_+, and τ' have been calculated from the method described in ref 26. For a series of copolymers with $f_B N_C = 70$ and homopolymers with $N_A = 84$ (PDMS1) and $N_B = 97$ (PI4), we obtained $f_A^{bal} = 0.48$, $\kappa_+ = 1.92kT$, and $\tau' = 0.270kT$ Å^{-1}. The prediction of eq 2 agrees extremely well with the results of three micelle simulations shown by open circles. The prediction of Leibler's strong-stretching theory for γ_{cmc},[30] which neglects swelling of the micelle core, is shown as a dotted line.

For sufficiently asymmetric copolymers, with $f_A \geq 0.66$, the SCFT predictions are remarkably consistent with the measured interfacial tensions. However, SCFT predictions of γ_{cmc} are significantly higher than the measurements, for $f_A < 0.6$, with a particularly large discrepancy for $f_A = 0.58$.

For the three samples with $0.6 \leq f_A \leq 0.63$, it was very difficult to obtain reproducible results, because the relaxation of the drop diameter became dramatically slower and dependent on copolymer concentration as shown in Figure 8 for IDMS7 ($f_A = 0.6$). In this case, the drop diameter continued to decrease throughout 3 days of observation, and the overall trends depended significantly upon the concentration of copolymer even above the apparent cmc. This transient behavior is very different from that observed for either $f_A \geq 0.66$ or $f_A \leq 0.58$ in Figure 3.

3.4. Dependence on Homopolymer Molecular Weight. An alternative way to control the spontaneous curvature of a monolayer is to change the relative lengths of the homopolymers. Here we examine the effect of varying molecular weight M_{PI} of PI on interfacial tension. We have measured the interfacial tension between the PDMS1 matrix that initially contains 0.1 wt % of the symmetric IDMS1 and a series of PI homopolymers of varying molecular weight.

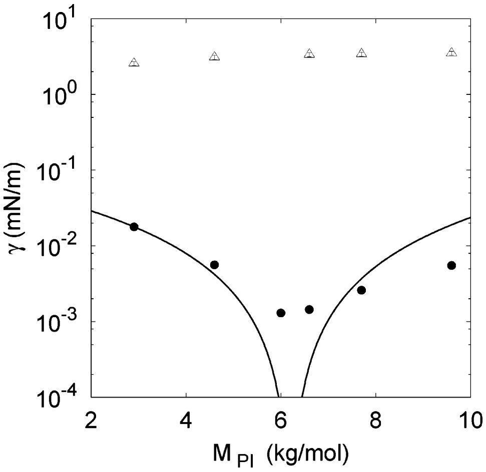

Figure 9. Interfacial tension γ in the system of PDMS1/PI/IDMS1 as a function of molecular weight of PI. Filled circles are values of γ in ternary systems with 0.1 wt % IDMS1. Open triangles are corresponding values for bare PDMS1/PI interfaces, with no copolymer surfactant.

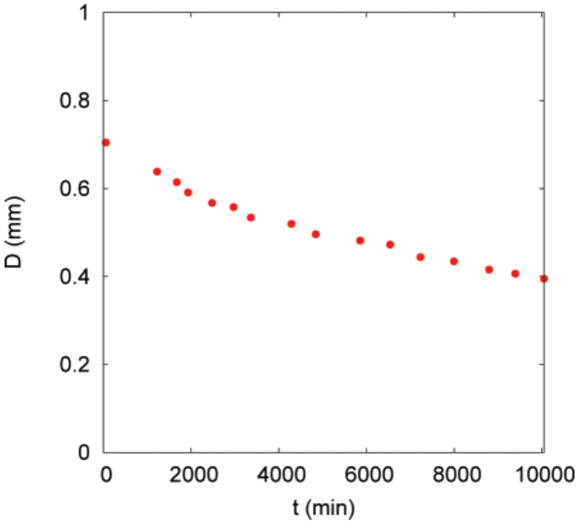

Figure 10. Variation of the diameter of the PI5 drop in the PDMS2 matrix at a concentration of 0.2 wt % of IDMS13. The rotational frequency is 6300 rpm.

The results, which are shown in Figure 9, exhibit an essentially quadratic dependence on M_{PI}, with a very low minimum in γ at a balance point between 6K and 6.6K. The solid line is an approximate SCFT prediction of the form $\gamma = (\tau'^2/2\kappa_+)(\beta - \beta^{bal})^2$ analogous to eq 2, in which $\beta = N_{PI}/N_{PDMS}$ and $\tau' \equiv \partial\tau/\partial\beta$. The displayed prediction uses parameters $M_{PI}^{bal} = 6.2$K, $\kappa_+ = 2.00kT$ and $\tau' = 0.0237kT$ Å^{-1} that were all obtained from a separate series of SCFT calculations.

3.5. A Larger Copolymer. Another series of measurements were carried out with IDMS13 copolymer, PDMS2 matrix, and PI homopolymers of varying molecular weight. IDMS13 is a symmetric copolymer with a molecular weight nearly twice that of IDMS1, which thus has a core block molecular weight $M_{PI} = 9.3$K, roughly twice that of any of the other copolymers used in our experiments. IDMS13 was initially added to the PDMS2 matrix at a concentration of 0.2 wt %.

In spinning drop experiments with IDMS13, equilibration of the drop size was dramatically slower than that in experiments with the smaller copolymer IDMS1. Figure 10 shows the time dependence of the drop diameter in a system with PDMS2 and PI5 homopolymers, and IDMS13 copolymer. In this example, the drop diameter was still decreasing at a noticeable rate after 1 week. No reliable data could thus be obtained for the steady-state interfacial tension.

This dramatic difference in the time required to establish a steady-state drop size (less than an hour vs at least 1 week) is too large to be explained as a direct consequence of the difference in the diffusivity of free copolymer molecules in either of the two phases, or of spherical micelles in PDMS. The diffusivity of molecularly dissolved IDMS13 in either PI or PDMS is predicted by the Rouse model to be about half the corresponding diffusivity of IDMS1, due to the factor of 2 difference in molecular weight. The diffusivity of spherical micelles, which is predicted by the Stokes−Einstein equation to be inversely proportional to the micelle hydrodynamic radius, is expected to decrease by less than a factor of 2 over the same range of molecular weights. No argument that relates the time required to equilibrate the drop size to the time for either molecules or spherical micelles to diffuse a constant or nearly constant distance can explain the observed difference in time scales.

4. Diffusion Limitations

In this section, we consider the kinetics of copolymer diffusion in the spinning drop tensiometer. Our discussion is based on an analysis of copolymer diffusion to a polymer−polymer interface given in ref 22.

This analysis assumes that the rate of accumulation of copolymer is controlled by diffusion, rather than by limitations either on the rate at which micelles can be destroyed at or near the interface, or on the rate at which free copolymer can adsorb to a crowded interface. It was shown in ref 22 that, if transport is indeed diffusion limited, the chemical potential of copolymer at the interface can reach the equilibrium value characteristic of a micellar solution as long as either of two conditions is satisfied. First, if the experiment allows time for free copolymer to diffuse throughout the drop, the system can reach a state of true global equilibrium, in which the copolymer chemical potential becomes homogeneous throughout the system. Second, even if the experiment allows too little time for global equilibration, an equilibrium interfacial concentration can nonetheless be obtained during an intermediate time regime (greater than that required to accumulate an interfacial copolymer monolayer) if the flux of copolymer into the drop remains small enough so that it does not deplete the copolymer concentration in the matrix near the interface below the cmc.

In appendix A.3, we estimate the time required for copolymer that diffuses into the PI drop to reach the center of the drop. Specifically, we estimate the time for free copolymer to diffuse throughout a long cylinder with a radius equal to the final radius obtained in the spinning drop experiment. In a spinning drop tensiometer, at any specified angular velocity, the radius of the drop depends upon the interfacial tension, and decreases with decreasing interfacial tension. We find that the required diffusion time is of order 10 h for systems with a measured interfacial tension of $\gamma \sim 10^{-2}$ mN/m, and is several hours even for the lowest observed value of $\gamma \sim 10^{-3}$ mN/m. In our experiments on systems with added copolymer, the drop is observed to approach its final diameter with a relaxation time of order 10 min. This time is nearly the same for symmetric copolymers, which exhibit a similar solubility in both phases, and strongly asymmetric copolymers, which are essentially insoluble in the PI drop. We thus conclude that the observed relaxation time is unrelated to the time required for copolymer to diffuse throughout the drop, and is presumably related instead to the time required to initially accumulate a monolayer along the interface.

In appendix A.4, we analyze the question of whether the diffusive flux of copolymer into the drop is large enough to deplete the copolymer concentration below the cmc near the interface within the PDMS. We conclude that it is not: The concentration is predicted to remain above the cmc throughout the PDMS matrix. In experiments with highly asymmetric copolymers, this prediction is primarily a result of the fact that, for $f_A > 0.6$, the copolymer becomes almost insoluble in the PI. In experiments with nearly symmetric copolymers, it is instead primarily a result of the fact that the monomeric friction coefficients in PDMS are much lower than those in PI, so much so that the estimated diffusivity of micelles in PDMS is actually slightly greater than the estimated diffusivity of molecular dissolved copolymer in PI. As a result, we find that micellar diffusion in the PDMS is generally sufficient to supply the flux of copolymer that diffuses into the PI, and thereby maintain a concentration above the cmc near the interface. If the flux to the interace is controlled by diffusion (rather than by limitations on the rate of micelle dissolution or interfacial adsorption), then an equilibrium interfacial tension should be obtained in our experiments.

5. Discussion

While many of our experimental results agree well with relevant theoretical predictions, two mysteries remain. The first is the anomalously low interfacial tension obtained for $0.5 < f_A \lesssim 0.6$, and rapid change in γ as a function of f_A for $f_A \simeq 0.6$. The second is the extremely long time required for the drop diameter to reach a steady state in systems containing the longer symmetric IDMS13 copolymer. Possible reasons for these results are discussed below.

5.1. Low γ for Nearly Symmetric Copolymers. The observed dependence of γ on f_A between 0.5 and 0.63 is distinctly different from the parabolic dependence predicted by the equilibrium theory of ref 17. This could in principle be the result either of an equilibrium phenomenon that is not accounted for in that theory, or of a kinetic phenomenon.

We were initially tempted to interpret the rapid change in γ near $f_A = 0.6$ as an equilibrium phenomenon that is somehow related to the appearance of a bicontinuous microemulsion and the appearance of three phase coexistence. The equilibrium theory of ref 17 assumed the existence of a phase of swollen spherical micelles in two-phase coexistence with an excess phase of nearly pure PI. Systems with balanced surfactants, such as symmetric diblocks, often instead form a bicontinuous microemulsion in three phase coexistence with two excess phases. To determine whether a bicontinuous microemulsion phase might be formed in some of the systems studied here, we also studied the phase behavior of mechanically blended ternary mixtures (PDMS1/PI4/IDMS3 and PDMS2/PI5/IDMS13) containing equal volumes of PI and PDMS homopolymers and varying amounts of symmetric block copolymers. Both optical examination and small-angle X-ray scattering (SAXS) experiments[27] confirm that these mixtures form a lamellar phase at high surfactant concentrations and a bicontinuous microemulsion at lower concentrations and that the microemulsion exhibits coexistence with excess homopolymer phases of PI and/or PDMS.

The phase behavior observed for these ternary mixtures is completely consistent with the behavior observed in small molecule mixtures of oil, water, and nonionic poly(alkyl-*b*-ethylene oxide) surfactant near their balance temperature T_b at which the monolayer spontaneous curvature vanishes. To assess any explanation of the observed dependence of γ_{cmc} on f_A that appeals to purely equilibrium phenomena, it is thus important to first compare our observations to those obtained in careful experiments on these small molecule analogs. In the small molecule mixtures, the spontaneous curvature of the monolayer depends strongly upon temperature T, which plays a role analogous to that played here by the block ratio f_A (This analogy is discussed in more detail in ref 17). The dependence on f_A observed in subsection 3.3 is, however, quite different from the dependence on T observed in the small molecule mixtures. In the small molecule mixtures, a region of three phase coexistence between a bicontinuous microemulsion phase and oil- and water-rich phases opens over a relatively narrow range of temperatures $T_l < T < T_u$ centered around the balance temperature. The interfacial tension between oil- and water-rich phases is, however, found to be a continuous, nearly quadratic function of temperature, with no discontinuity at T_l or T_u. After considering what is known about these systems, and the underlying thermodynamic reasons for the observed continuity of the interfacial tension at T_l and T_u, we concluded that it was hard to imagine a hypothesis that could plausibly explain why the *equilibrium* interfacial tension should instead be a discontinuous function of f_A in the systems studied here.

We must thus also consider what kinetic phenomena may be relevant. The analysis given in ref 22, which is the basis of the analyis given in the appendix, attempts to account only for the effects of diffusion limitations upon the observed interfacial coverage. That analysis ignored any limitations on the rate at which micelles can be destroyed at or near the interface, on the rate of interfacial adsorption, or on the rate at which micelle cores can swell by absorbing dissolved PI homopolymer as they approach the interface. Limitations on the rates of either of the first two processes (micelle dissolution and interfacial adsorption) would tend to decrease the interfacial coverage, and thereby increase the interfacial tension. Limitations on the rate of emulsification of PI by micelles could instead tend to decrease the observed interfacial tension, as discussed below:

Micelles in the PDMS phase must be unswollen sufficiently far from the interface, where no PI is present. They would have to absorb PI homopolymer dissolved in the PDMS matrix in order to reach the swollen equilibrium structure predicted by SCFT calculations. In systems of nearly symmetric copolymers, in which the copolymer retains some solubility in PI, micelles must be destroyed at or near the interface in order to compensate the continual loss of copolymer into the PI phase. If micelles were unable to swell to their equilibrium core radius before being destroyed, the chemical potential of copolymers within the micelles would be higher than that predicted for a fully swollen micelle. If the chemical potential at the interface were in equilibrium with that obtained in the resulting unswollen or partially swollen micelles, this would result in a higher interfacial coverage of copolymer, and thus a lower interfacial tension, than that obtained in equilibrium.

The scenario described above is similar to one assumed implicitly in an early theoretical study by Leibler.[30] Leibler used a simple strong stretching theory to calculate the equilibrium interfacial tension of an interface between a phase containing AB diblock copolymers in A homopolymer and a phase of pure B homopolymer, but neglected any swelling of the micelle cores. As a result of this neglect, he predicted a vanishing interfacial tension for nearly symmetric copolymers, over a range of $0.31 < f_A < 0.69$, rather than the quadratic dependence on f_A. Our experimental results resemble Leibler's predictions, insofar as we obtain an interfacial tension lower than that predicted for swollen micelles of nearly symmetric copolymers. The range of values of f_A in which the measured tension falls below the predictions corresponds roughly to that in which the core is predicted to swell significantly, and also to that in which the copolymer retains a non-negligible solubility in PI, leading to a nonzero net rate of micelle destruction. We thus conjecture that the interfacial tension could be reduced below its equilibrium value in these systems by a limitation on the rate at which micelles can swell before being destroyed, due to the low solubility of PI homopolymer in the PDMS matrix.

5.2. Slow Equilibration for a Longer Copolymer. While experiments with copolymers with a core block size $M_{PI} \simeq 5K$ resulted in reasonably rapid equilibration of the drop diameter, over times of order 10−20 min, our experiments with an IDMS13 copolymer with $M_{PI} = 9.3K$ resulted in dramatically longer equilibration times, of greater than 10^4 min. We assume that the slow rate of mechanical equilibration reflects a slow rate of accumulation of copolymer at the interface. As already noted, this large a difference in equilibration times cannot be explained as a direct consequence of an decrease in the diffusivity of either free molecules or spherical micelles.

One explanation that we have considered is that the increase in equilibration time might be the result of a change in the primary mechanism of copolymer transport from free copolymer diffusion to micellar diffusion, as a result of a dramatic decrease in the cmc with increasing molecular weight. Because the cmc depends exponentially on the molecular weight of the copolymer core block, doubling the PI core block length from 5K to 10K is expected to decrease the cmc by many orders of magnitude, causing IDMS13 to become essentially insoluble in PDMS as a unimer. Theoretical estimates of the time τ_{acc} required to accumulate a saturated interfacial monolayer are given in appendix A.2 for both short and long diblocks. These estimates are based on the theory of ref 22, which allows for both free copolymer and micellar diffusion, but ignores any limitations on the rates at which micells can dissolve. The theory suggests that (in the absence of limitations on the rate of micelle dissolution), the flux of the shorter IDMS1−IDMS12 diblocks to the interface would be controlled by the rate of single-molecule diffusion across a zone near the interface, while the flux of IDMS13 copolymer to the interface would be controlled by micellar diffusion. We predict an accumulation time τ_{acc} of roughly 3 min for an the shorter IDMS1 copolymer with an initial volume fraction 0.2%, and $\tau_{acc} \sim 20$ min for the longer IDMS13 copolymer at the same initial concentration. The predicted time scales are surprisingly similar, despite the change in transport mechanism, for two reasons: First, the predicted micellar diffusivity of either copolymer in PDMS is only about 1 order of magnitude less than the tracer diffusivity of IDMS1 in PDMS, because the single-molecule diffusivity is reduced by the large friction coefficient of the exposed PI block. Second, the available concentration of copolymer in micelles is always higher than the concentration ϕ_{cmc} of free copolymers, even for the shorter copolymers. This modest difference in predicted accumulation times is not sufficient to explain the observed difference in drop equilibration times.

The increase in equilibration times could be the result of a dramatic decrease in the rate at which micelles dissolve at or near the interface with increasing copolymer molecular weight. Semenov theoretically estimated the kinetic barrier to the destruction of micelles at the cmc and showed that this barrier can become prohibitively large ($\gg 10kT$) for high molecular weight polymers, causing a very slow dissolution.[9] This barrier is a strongly increasing function of molecular weight. Similar comments probably also apply to the barrier to the dissolution of micelles at (rather than near) an unsaturated interface, though this type of interfacial reaction has not been analyzed separately. Because the molecular weight dependent barrier is related to the rate of micelle dissolution by an Arrhenius factor, it is quite plausible for the dissolution of micelles at or near an interface to be relatively rapid in experiments involving low molecular weight copolymers and to become prohibitively slow when the molecular weight is increased by a factor of 2. This seems to us the most likely cause.

6. Conclusions

We have used a spinning drop tensiometer to measure interfacial tensions of PI/PDMS interfaces with adsorbed IDMS diblock copolymers. We have characterized three different series of systems: one with a series of low molecular weight copolymers (5K PI block) of varying composition and nearly symmetric homopolymers, one with a symmetric copolymer and the PI homopolymers of varying molecular weight, and one with a nearly symmetric copolymer of somewhat higher molecular weight and PI homopolymers of varying molecular weight. For all of the systems studied, the IDMS copolymer is expected to be more soluble in the PDMS matrix, and to form micelles in PDMS but not in the PI drop. The copolymer was always premixed with the PDMS.

Measured interfacial tensions at copolymer concentration above the apparent cmc have been compared to SCFT predictions that assume the existence of swollen spherical micelles in the PDMS matrix. These predictions agreed extremely well with our measurements using sufficiently asymmetric copolymers, with $0.66 \leq f_A \leq 0.73$. In systems with symmetric copolymers, with $f_A \simeq 0.5$, we observe ultralow interfacial tensions, $\gamma \simeq 10^{-3}$ mN/m. This behavior is consistent with theoretical predictions of very low interfacial tensions for symmetric systems, and with observations of ultralow tensions in balanced small molecule systems. However, such low interfacial tensions had never previously been measured in a polymeric system.

For slightly asymmetric copolymers, with $0.5 < f_A < 0.60$, measured values of γ are noticeably lower than our SCFT predictions. The interfacial tension also changes rapidly with f_A over a narrow range of values of $f_A = 0.6-0.63$, over which γ changes by an order of magnitude. Within this range, we were unable to obtain reliable values of equilibrium interfacial tension, because the drop diameter was found to slowly decrease over very long times, in a manner that depends upon copolymer concentration. We suggest that the anomalously low values of γ obtained for nearly symmetric copolymers could be the result of a limitation in the rate at which micelles in the PDMS phase can emulsify PI homopolymer as they approach the interface.

Experiments with a higher molecular weight copolymer (IDMS13) showed a dramatically slower relaxation of the drop size than observed with IDMS1, making it impossible for us to obtain reliable measurements of equilibrium interfacial tension. We suggest that this could be the result of dramatic decrease with increasing molecular weight of the rate at which micelles can be destroyed at or near the interface.

Acknowledgment. We would like to thank Prof. Daniel Joseph in the Aerospace Engineering and Mechanics Department of the University of Minnesota for allowing our extensive use of his spinning drop tensiometer, and Laura Copp and Zachary Wilcock for assistance with these measurements. This work was supported by the Industrial Partnership for Research in Interfacial and Materials Engineering (IPRIME) at the University of Minnesota, the RTP company, and the Minnesota Supercomputing Institute (MSI).

Appendix A. Analysis of Copolymer Diffusion

In this appendix, we quantitatively analyze the kinetics of diffusion of copolymer to, and sometimes through the PI−PDMS interface in our experiments. In subsection A.1, we present estimates of the tracer diffusivities of IDMS copolymers in PI and PDMS matrices, and of the diffusivity of IDMS micelles in PDMS. In A.2, we estimate the time required to accumulate a saturated monolayer of surfactant on an initially bare PI−PDMS interface. In A.3, we estimate the time required for copolymer that dissolves in PI to diffuse throughout the PI drop. In A.4, we consider whether this diffusion of copolymer into the PI drop could deplete the concentration of copolymer near the interface in the PDMS below the cmc.

A.1. Estimating Diffusivities. To estimate the tracer diffusivities of IDMS copolymers in both PI and PDMS, we use the Rouse model to predict the dependence on the block molecular weights, and (when necessary) the Lodge−McLeish model to predict the dependence of friction coefficients on the nature of the surrounding material. The diffusivity of IDMS copolymer in either PI or PDMS is of the form $D_f = kT/(N_{PI}\zeta_{PI} + N_{PDMS}\zeta_{PDMS})$, where ζ_{PI} and ζ_{PDMS} are the monomeric friction coefficients for PI and PDMS, respectively, in the homopolymer of interest.

We first consider the diffusivity of IDMS copolymer in PI. A simplified estimate of this quantity may be obtained by noting that the reported friction coefficient $\zeta_{PI}(PI) = 1.5 \times 10^{-6}$ dyn s/cm of pure PI in PI at 298 K[34,35] (defined using a reference volume of 99 cm^3/mol) is several hundred times greater than the friction coefficient of $\zeta_{PDMS}(PDMS) = 7.5 \times 10^{-9}$ dyn s/cm of pure PDMS at 298 K[32,33] (expressed here using the same reference volume). As a result, the total friction of a nearly symmetric IDMS copolymer in PI is expected to be dominated by the friction of the PI block. Ignoring the friction of the PDMS block yields a diffusivity of $D_f^{PI} = kT/(N_{PI}\zeta_{PI}) \simeq 5 \times 10^{-10}$ cm^2/s for a copolymer with a PI block of length 4800 g/mol. A refined estimate based on the Lodge−McLeish model (discussed below) yields a negligible friction coefficient of $\zeta_{PDMS}(PI) = 1.8 \times 10^{-8}$ dyn s/cm for PDMS in PI, and an essentially identical estimate of $D_f^{PI} = 5.1 \times 10^{-10}$ cm^2/s for the diffusivity of a 4800(PI)-5100(PDMS) g/mol IDMS1 copolymer.

The diffusivity of an IDMS copolymer in PDMS can also be estimated by assuming that the total friction is dominated by the friction of the PI block. The Lodge−McLeish model has been used to estimate the monomeric friction coefficient ζ_{PI}(PDMS) of PI in PDMS. By using the PI self-concentration of $\phi_s^{PI} = 0.45$ given in ref 34 and the Fox equation $1/T_{g,eff}^{PI}(PDMS) = \phi_s^{PI}/T_g^{PI} + (1 - \phi_s^{PI})/T_g^{PDMS}$, we obtain an effective glass transition temperature of $T_{g,eff}^{PI}(PDMS) = 173$ K for a PI tracer in PDMS. A friction coefficient $\zeta_{PI}(PDMS) = 1.2 \times 10^{-7}$ at 298 K is then obtained from the WLF equation, using the procedure and WLF parameters $C_1{}^g = 10.8$, $C_2{}^g = 51.1$ K and $\zeta_g{}^o = 5.6$ dyn s/cm for pure PI given in ref 35. An analogous calculation was used to estimate the friction coefficient of PDMS in PI (which we found to be negligible compared to that of PI in PI block), using a calculated self-concentration of $\phi_s^{PDMS} = 0.43$ and published WLF coefficients.[36]

The diffusion coefficient D_m for spherical micelles in PDMS can be estimated from the Stokes−Einstein equation $D_m = kT/6\pi\eta_o R$, in which η_0 is the PDMS matrix viscosity, and R is the hydrodynamic radius of a micelle. We have estimated hydrodynamic radii from the results of SCFT simulations of micelles for a series of $f_B\chi N = 12$ with the homopolymers of equal length $N_A = N_B = f_B N_C$, which are similar to the series of PI/PDMS/IDMS systems discussed in subsection 3.3. The hydrodynamic radius has been taken (somewhat arbitrarily) to be the radius at which the local volume fraction of the copolymer corona block drops to 10%. In Figure 11, we show predictions for the radii

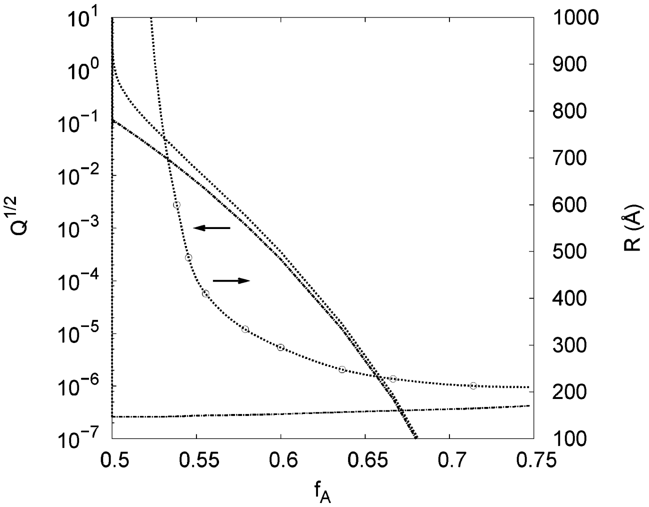

Figure 11. Calculated dimensionless ratio $Q^{1/2}$ and the hydrodynamic radii of swollen micelles (dotted lines) and unswollen micelles (dot dashed lines) as functions of f_A for a series of polymers with $f_B N_C = N_A = N_B = 70$ and $\chi N_C f_B = 12$.

both of swollen micelles in a two-phase ternary system, in which PI is emulsified in the core of each micelle, and of unswollen micelles in binary mixtures of the copolymer and PDMS, without PI.

The predicted radius of a swollen micelle diverges as f_A approaches 0.5, causing the predicted micelle diffusivity to approach zero. The assumption that the copolymer forms spherical micelles that reach their thermal equilibrium radius is, however, dubious in this limit, both because of kinetic constraints on the amount of PI that can be absorbed by micelles before they are destroyed, since the PI must diffuse through the PDMS matrix to reach the micelles, and because the equilibrium structure in this parameter regime appears to be a bicontinuous rather than a droplet microemulsion.

A.2. Accumulation of a Monolayer. We now estimate the amount of time required to accumulate a nearly saturated copolymer monolayer by diffusion of copolymer from PDMS to the interface. In the spinning drop experiment, the dynamics of interfacial adsorption is complicated by the fact that the interfacial area of the drop increases in response to decreases in interfacial tension, thus tending to slow the increase in adsorbed copolymer per area. In addition, the accumulation of a monolayer could be slowed by limitations on the rate at which micelles can dissolve at or near the interface. Here, we estimate the time required to accumulate a nearly saturated monolayer at a hypothetical interface of fixed area, in the diffusion-controlled limit of fast micelle dissolution. The resulting prediction is thus expected to underestimate somewhat the time required for the drop to equilibrate, and to underestimate it dramatically if the rate of accumulation is actually controlled by the rate of micelle dissolution.

In ref 22, it is shown that, if micelle dissolution and interfacial adsorption are rapid at the cmc, transport of copolymer to an initially bare interface must generally occur by a combination of free copolymer and micellar diffusion: The copolymer must be transported by free copolymer diffusion across an "exclusion zone" near the interface, in which the copolymer concentration falls below the cmc, but must be transported to the edge of this zone by micellar diffusion alone. The time required to accumulate an interfacial monolayer may be controlled by either free molecule or micellar diffusion and may be approximated by the smaller of the time estimates obtained from two complementary approximations. In the first approximation, micelle diffusivity is assumed to be negligible, in which case the flux to the interface is controlled by the rate of free copolymer diffusion across an exclusion zone. In the second approximation, the cmc is assumed to be negligible, in which case the flux is controlled by micellar diffusion.

In the limit of negligible micelle diffusivity, but non-negligible cmc, the flux to the interface is equal to the rate at which micelles are dissolved along the moving edge of an exclusion zone. The width $h(t)$ of this zone was shown[22] to initially increase as $h(t) = \sqrt{2D_f^{PDMS}\phi_{cmc}/\phi_{m0}}$, where D_f^{PDMS} is the free copolymer diffusivity in PDMS, and $\phi_{m0} \equiv \phi_C - \phi_{cmc}$ is the initial volume fraction of copolymers in micelles in PDMS. We consider the evolution of the excess volume $\Gamma(t)$ of adsorbed copolymer per unit area of interface. This quantity has units of length, and was denoted z_i^* by Shull, Kramer and co-workers.[37−39] In the limit discussed here, $\Gamma(t)$ is given by the product $\Gamma(t) = \phi_{m0}h(t)$. Equating $\Gamma(t = \tau_{acc})$ with the equilibrium value Γ_{cmc} obtained above the cmc yields an estimated accumulation time

$$\lim_{D_m \to 0} \tau_{acc} = \frac{{\Gamma_{cmc}}^2}{2D_f^{PDMS}\phi_{cmc}\phi_{m0}} \tag{3}$$

Using an estimated interfacial excess of $\Gamma_{cmc} \simeq 6$ nm (which we obtained from SCFT for a symmetric diblock similar to IDMS1 in PI4/PDMS1), $\phi_{cmc} = 0.0003$ (which we obtain from Figure 5), and a diffusivity $D_f^{PDMS} = 6.1 \times 10^{-9}$ cm^2/s (estimated in appendix A.1), we predict $\tau_{acc} = 2.3$ min for $\phi_C = 0.001$ and $\tau_{acc} = 1.0$ min for $\phi_C = 0.002$.

In the opposite limit of negligible cmc but non-negligible micellar diffusivity, the flux to the interface approaches the diffusive flux of an initially homogeneous distribution of micelles to an absorbing boundary. This yields an interfacial coverage $\Gamma(t) = \phi_C\sqrt{2D_m t/\pi}$, in which D_m is the diffusivity of micelles in PDMS. Setting $\Gamma(t) = \Gamma_{cmc}$ yields an accumulation time

$$\lim_{\phi_{cmc} \to 0} \tau_{acc} = \frac{{\Gamma_{cmc}}^2}{2D_m{\phi_{m0}}^2} \tag{4}$$

Taking $\Gamma_{cmc} = 6$ nm and $D_m = 10^{-9}$ cm^2/s yields $\tau_{acc} = 19.2$ min for $\phi_C = 0.001$ and $\tau_{acc} = 3.2$ min for $\phi_C = 0.002$.

These estimates suggest that, in our experiments with IDMS1−IDMS12, accumulation of copolymer at the interface is controlled primarily by molecular diffusion across an exclusion zone, though micellar diffusion is not completely negligible. The predicted accumulation times of $\tau_{acc} = 1 - 2$ min for $\phi_C = 0.001$ - 0.002 are somewhat less than our estimated drop equilibration time of 10−20 min. This relatively small discrepancy could be the result of an inaccuracy in our estimate of the tracer diffusivity of IDMS in PDMS, which has not been independently measured, or a result of the limitations of our model (e.g., our assumption of very fast micelle dissolution reactions). It could also easily be the result of inaccuracy in our estimate of the drop equilibration time, due to a lack of drop diameter data at early times in systems with added copolymer. Further experiments that focus on the evolution of the drop diameter at early times in the presence of a copolymer additive would be useful.

Similar reasoning can be used to estimate τ_{acc} for experiments with the longer IDMS13 copolymer. Because $\phi_{cmc} \propto e^{-\chi N_{PI}}$, the predicted cmc for IDMS13 is extremely low, $\phi_{cmc} \sim 10^{-9}$. Copolymer transport is thus controlled in this case by micellar

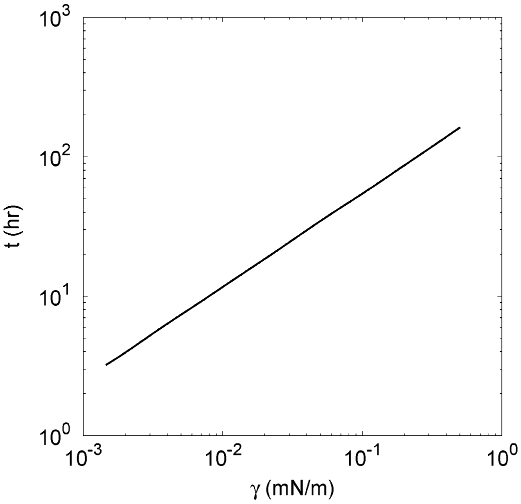

Figure 12. Time t for copolymer to diffuse to the center of a drop in a spinning drop tensiometer as a function of interfacial tension γ. The drop diameter $d(\gamma)$ is taken to be the final diameter of a PI drop in a PDMS matrix rotating at 6300 rpm.

diffusion. Neither the micelle diffusivity D_m for this longer copolymer nor the effective interfacial thickness Γ_{cmc} are expected to differ dramatically from those of the smaller IDMS1−IDMS12 copolymers in the same PDMS matrix. If we assume, for simplicity, that both the micelle hydrodynamic radius and Γ_{cmc} increase as roughly $\sqrt{N}$, we obtain an estimate of τ_{acc} for IDMS13 that is larger than that obtained for IDMS1 in the limit $\phi_{cmc} \rightarrow 0$ by only a factor of $2\sqrt{2}$, giving $\tau_{acc} \sim 50$ min for $\phi_C = 0.001$ and $\tau_{acc} \sim 10$ min for $\phi_C = 0.002$. These estimates are too small, and too similar to our estimates for the smaller copolymers, to explain the observed drop relaxation times of greater than 10^4 min for systems with IDMS13. Possible explanations of this discrepancy are discussed in section 5.

A.3. Diffusion Through the PI Drop. We next consider whether the time scale of our experiments allows sufficient time for free copolymer to diffuse from the PI/PDMS interface to the center of the PI drop. The time for copolymer to diffuse from the interface to the center of a long cylindrical droplet of diameter d is given by

$$t = d^2/4kD_f^{PI} \tag{5}$$

where k is a numerical prefactor. We obtain a value of $k = 5.8$ by taking t to be the relaxation time of the slowest decaying eigenmode in an expansion of the concentration field in an infinite cylinder in terms of zeroth order Bessel functions (i.e., the first zero of the Bessel function $J_0(kR)$ occurs at $(kR)^2 = 5.8/R^2$). We take the drop diameter d in eq 5 to be the final diameter of the drop in a spinning drop tensiometer, which is given in eq 1 as a function of interfacial tension γ, rotation rate ω, and the density difference $\Delta\rho$. Figure 12 shows the characteristic time t as a function of γ that is obtained from eq 5 for a drop of diameter $d(\gamma)$ calculated with eq 1, using a rotation rate of 6300 rpm typical of our experiments and the measured PI/PDMS density difference. This figure demonstrates that only systems containing very nearly symmetric copolymers, with $\gamma < 0.01$ mN/m, might have time to diffuse to the center of the drop within an experimental time scale of order 10 h.

A.4. Depletion of Interfacial Coverage. We now consider the question of whether the interfacial tension measured after the drop diameter has stabilized corresponds to the equilibrium value obtained at concentrations above the cmc. We assume that the relevant time regime is an intermediate regime of times much less than that required for copolymer to diffuse throughout the drop but greater than that required to accumulate a nearly time-independent interfacial coverage. As shown in ref 22, the interfacial tension will generally reach a time-independent value during this time regime. This value may, however, correspond either to the equilibrium value above the cmc, if the $\phi_C > \phi_{cmc}$ in PDMS near the interface, or to a higher nonequilibrium value, if $\phi_C < \phi_{cmc}$ near the interface as a result of a depletion caused by continuing diffusion of copolymer into the drop. The choice between these scenarios is determined by the value of a dimensionless parameter

$$Q = \frac{D_f^{PI}}{D_m^{PDMS}}\left(\frac{\phi_{cmc}}{\phi_{m0}K}\right)^2 \tag{6}$$

where $K \equiv \phi_C^{PDMS}/\phi_C^{PI}$ is the partition coefficient relating the concentrations of free copolymer on the PDMS and PI sides of the interface. If $Q > 1$, the concentration of free copolymer near the interface will be depleted below the cmc, resulting in a nonequilibrium interfacial tension. Note that $Q < 1$ will always be obtained in the limit $K \rightarrow \infty$ in which the copolymer becomes insoluble in the drop.

The partition coefficient K can be derived from Flory−Huggins theory, which yields

$$\ln K \simeq \chi N_c(f_A - f_B) + N_C\left(\frac{1}{N_A} - \frac{1}{N_B}\right) \tag{7}$$

For systems similar to those studied here, in which a copolymer with $\chi N_C f_B = 12$ is mixed with symmetric homopolymers of length $N_A = N_B = N_C f_B$, we obtain a partition coefficient $K = 1$ at $f_A = 0.5$, and $K = 457$ at $f_A = 0.6$. For $f_A \gtrsim 0.6$, the copolymer becomes essentially insoluble in PI.

Our results for $Q^{1/2}$ as a function of f_A are shown in Figure 11, for a set of systems similar to IDMS1−IDMS12. For unswollen micelles, $Q < 1$ for all values of f_A. The fact that $Q \ll 1$ for very asymmetric copolymers is a reflection of the fact that sufficiently asymmetric copolymers become insoluble in PI, or that $K \gg 1$. For swollen micelles, the divergence of the micelle radius as $f_A \rightarrow {}^1/_2$ causes the micelle diffusivity to vanish, and thus causes Q to diverge in this limit. Despite this, however, we find $Q > 1$ for swollen micelles only for a very narrow range $|f_A - 0.5| < 0.001$. If we ignore the predictions for almost perfectly symmetric copolymers (which yield $Q > 1$ only if we take seriously the idea that copolymer will form enormously swollen spherical micelles), the above analysis suggests that the copolymer concentration in PDMS should never be depleted below the cmc by diffusion into the drop.

References and Notes

(1) Safran, S. A. *Statistical Thermodynamics of Surfaces, Interfaces, and Membranes*; Westview: Boulder, CO, 2003.
(2) Kahlweit, M.; Strey, R. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 654.
(3) Kahlweit, M.; Strey, R.; Busse, G. *Phys. Rev. E* **1993**, *47*, 4197.
(4) Strey, R. *Colloid Polym.* Sci. **1994**, *272*, 1005.
(5) Sottmann, T.; Strey, R. *J. Chem. Phys.* **1997**, *106*, 8606.
(6) Bates. F. S.; Maurer, W.; Lipic, P. M.; Hillmyer, M. A.; Almdal, K.; Mortensen, K.; Fredrickson, G. H.; Lodge, T. P. *Phys. Rev. Lett.* **1997**, *79*, 849.
(7) Hillmyer, M. A.; Maurer, W. W.; Lodge, T. P.; Bates, F. S. *J. Phys. Chem. B* **1999**, *103*, 4814.
(8) Washburn, N. R.; Lodge, T. P.; Bates. F. S. *J. Phys. Chem. B* **2000**, *104*, 6987.
(9) Jeon, H. S.; Lee, J. H.; Newstein, M. C. *Macromolecules* **1998**, *31*, 3340.
(10) Lee, J. H.; Ruegg, M. L.; Balsara, N. P.; Zhu. Y.; Gido, S. P.; Krishnamoorti, R.; Kim, M.-H. *Macromolecules* **2003**, *36*, 6537.

(11) Anastasiadis, S. H.; Gancarz, I.; Koberstein, J. T. *Macromolecules* **1989**, *22*, 1449.
(12) Hu, W.; Koberstein, J. T.; Lingelser, J. P.; Gallot, Y. *Macromolecules* **1995**, *28*, 5209.
(13) Jorzik, U.; Wolf, B. A. *Macromolecules* **1997**, *30*, 4713.
(14) Retsos, H.; Margiolaki, I.; Messaritaki, A.; Anastasiadis, S. H.; *Macromolecules* **2001**, *34*, 5295.
(15) Welge, I.; Wolf, B. A. *Polymer* **2001**, *42*, 3467.
(16) Retsos, H.; Anastasiadis, S. H.; Pispas, S.; Mays, J. W.; Hadjichristidis, N. *Macromolecules* **2004**, *37*, 524.
(17) Chang, K.; Morse, D. C. *Macromolecules* **2006**, *39*, 7746.
(18) Chang, K.; Morse, D. C. *Macromolecules* **2006**, *39*, 7397.
(19) Vonnegut, B. *Rev. Sci. Instrum.* **1942**, *13*, 6.
(20) Joseph, D. D.; Arney, M. S.; Gillberg, G.; Hu., H.; Hultman, D.; Verdier, C.; Vinagre, T. M. *J. Rheol.* **1992**, *36*, 621.
(21) Joseph, D. D.; Arney, M.; Ma, G. *J. Colloid Interface Sci.* **1992**, *148*, 291.
(22) Morse, D. C. *Macromolecules*, in press.
(23) Ndoni, S.; Papadakis, C. M.; Bates, F. S.; Almdal, K *Rev. Sci. Instrum.* **1995**, *66*, 1090.
(24) Cavicchi. K. A.; Lodge, T. P. *Macromolecules* **2003**, *36*, 7158.
(25) Fetters, L. J.; Lohse, D. J.; Richter, D.; Witten, T. A.; Zerkel, A. *Macromolecules* **1994**, *27*, 4639.
(26) Kitade, S.; Ichikawa, A.; Imura, N.; Takahashi, Y.; Noda, I. *J. Rheol.* **1997**, *41*, 1039.
(27) Chang, K. Ph.D. Thesis, University of Minnesota, 2005.
(28) Cochran, E.; Morse, D. C.; Bates, F. S. *Macromolecules* **2003**, *36*, 782.
(29) Personal communication with K. Almdal, 2005.
(30) Leibler, L. *Makromol. Chem., Macromol.* Symp. **1988**, *16*, 1.
(31) Semenov, A. N. *Macromolecules* **1992**, *25*, 4967.
(32) Fleischer, G.; Appel, M. *Macromolecules* **1995**, *28*, 7281.
(33) Roberts, C.; Cosgrove, T.; Schmidt, R. G.; Gordon, G. V. *Macromolecules* **2001**, *34*, 538.
(34) Lodge, T. P.; McLeish, T. C. B. *Macromolecules* **2000**, *33*, 5278.
(35) Haley, J. C.; Lodge, T. P. *J. Rheol.* **2004**, *48*, 463.
(36) Ferry, J. D. *Viscoelastic Properties of Polymers*; Wiley: New York, 1980; Chapter 11.
(37) Shull, K. R.; Kramer, E. J. *Macromolecules* **1990**, *23*, 4769.
(38) Shull, K. R.; Kramer, E. J.; Hadziioannou, G.; Tang, W. *Macromolecules* **1990**, *23*, 4780.
(39) Dai, K. H.; Kramer, E. J.; Shull, K. R. *Macromolecules* **1992**, *25*, 220.

MA062277A