Direct Force and Friction Measurements Reflecting Structural Changes in Confined Diblock Copolymer Liquids

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ABSTRACT: We have measured the normal and shear forces for a symmetric polystyrene–polyisoprene (PS–PI) diblock copolymer liquid in toluene, a good solvent for both blocks, between two mica surfaces. The aim was to investigate the structure of the macromolecular liquid when confined between surfaces separated by molecular-sized distances. The surface forces apparatus was used for these studies, and the microstructure was manipulated by varying the fraction of diblock in solution. Measurements of the equilibrium normal force profiles (intermolecular force versus separation distance between the confining surfaces) were made. All of these normal force profiles exhibited monotonic repulsive behavior. We found that in the disordered regime, as the fraction of diblock was increased, the intermolecular forces became much longer-ranged. As the fraction of diblock was further increased to concentrations near the bulk order–disorder transition (ODT), the ranges of the force profiles unexpectedly collapsed to shorter distances. In a series of dynamic surface forces experiments, the frictional force required to slide steadily one surface past the other with the macromolecular liquid intervening was measured as a function of shear rate. The shearing results reflected the same pattern of behavior exhibited in the normal force experiments. We determined that the frictional force of the most concentrated liquid was distinctly lower than that of the disordered samples at all shear rates and attribute both the equilibrium and dynamic results to be reflective to the inherent structure of the liquid. We believe that the reduction in the range of the normal force profiles and the reduction in frictional forces at the highest concentrations reflect pretransitional ordering in the confined sample. Our results are discussed in terms of surface-induced ordering and composition fluctuations, which are not accounted for in the mean-field description of polymer phase behavior.

Introduction

The classical treatment of intermolecular forces postulates that two types of continuum interactions exist: electrostatic, which includes charge-bearing and polarization interactions, and van der Waals forces. When two solid surfaces confine a liquid on a length scale approaching molecular sizes, however, the fluid can no longer be treated as a structureless continuum. The finite molecular size and imposition of the surfaces modify the force profiles. The advent of sensitive direct force measurement techniques in the 1970s led to the recognition of a third class of forces, the so-called structural forces. Often these forces are referred to as solvation forces, or, if the solvent is water, hydration forces. As all molecules have a distinct size, structural forces are present in all systems at some length scale. The range over which they become important, however, depends on the characteristic size of the system.[1]

The surface forces apparatus, which will be discussed in more detail in the Experimental Section, provides a means to measure directly intermolecular forces between two molecularly smooth surfaces with a resolution of approximately 10 μN and a distance resolution of better than 3 Å. Systems studied with this device include, but are not limited to, simple liquids, both polar[1,2] and nonpolar,[3,4] hydrogen-bonding liquids,[1,5] thermotropic[6] and lyotropic[7,8] liquid crystals, bilayers and fluidized membranes,[9,10] aqueous electrolyte solutions,[11] linear polymer melts,[12] and tethered chains.[13] As the lamellar-forming diblock copolymer liquid we have studied is uncharged, we restrict our comments to materials exhibiting distinct structural forces without the influence of electrostatic or polarization forces.

For spherical molecules such as cyclohexane and toluene, the force–distance profile oscillates between attraction and repulsion, with periodicity equal to the molecular diameter.[1] This behavior is due to the stratification of the molecules, caused by the imposition of the confining surfaces. Structural forces such as these occur at very small separation distances, i.e., when the surfaces are separated by a distance of 10 molecular diameters or less. Similar oscillatory force profile behavior is observed with n-alkanes, but the characteristic period of oscillations corresponds to the width of the short-chain liquid molecules. The induced layering and resultant oscillatory force profile persist for this type of liquid until the chain length reaches approximately 20 carbon units.[4] Beyond this limit, and especially for branched chain molecules, the complexity of the structure negates the surface-induced layering, and this gives rise to a purely repulsive monotonic force profile. This type of behavior is typically exhibited by nonadsorbing, disordered polymers.[12]

Liquids with inherent structure, such as liquid crystals, also exhibit distinctive force–distance profiles that reveal much about the character of the material when confined. Measurements of a nematic liquid crystal[6] showed the action of three distinct components of structural forces. One resulted from elastic deformation in the liquid crystal and was observed only when the liquid crystal molecules were trapped under the influ-

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ence of a twist which was induced by orienting the molecules in different directions at the confining surfaces. The second was a purely repulsive, monotonic force due to enhanced ordering at the surfaces. A third force, observed when less than six layers were trapped between the surfaces, oscillated with a periodicity corresponding to the repeat distance of the layers. Similar information on the interlayer spacing distance was evidenced for an egg–lecithin lamellar mesophase system.[8]

In another study of lamellar mesophases, Kékicheff and co-workers[10] used information from force profiles to analyze the stabilization mechanisms of layered structures. This investigation of oil-swollen and water-swollen lamellae-forming systems showed that the oil-swollen system was stabilized by Helfrich undulation forces, while the stiffer water-swollen system relied on electrostatic and hydration forces for stabilization. From their data, they were able to extract the membrane layer compression modulus which manifested itself in observed layer fluctuations.

One class of diblock copolymer systems that has been the focus of intense study with the surface forces apparatus is tethered chains. In the surface forces experiments, these systems are commonly made using a diblock copolymer that possesses one block that adsorbs to the confining surfaces and another that remains exposed in the good solvent. Concentrations of copolymer in the range of 10–100 mg L^{-1} are typically used to create these structured systems. The crowding induced by the adsorption of the anchor block forces the nonadsorbing block to become strongly stretched away from the tethering point into the solvent. These so-called polymer brushes exhibit long-range, monotonically repulsive normal force profiles. Direct force measurement confirms that these systems are stretched to lengths much greater than the radius of gyration of the polymers.[13]

At concentrations much higher than those previously used to form polymer brushes, diblock copolymers dissolved in good solvents for both blocks may adopt ordered structures. This structuring arises from the delicate enthalpy–entropy balance that dictates the phase behavior of the system. In a mean-field picture, the order parameter ($\chi_{\mathrm{eff}}N$) can be manipulated to move the system between the ordered and disordered state; here χ_{eff} is an effective segment–segment interaction parameter and N the degree of polymerization. In the simplest approximation, $\chi_{\mathrm{eff}} = \phi\chi$, where ϕ is the polymer volume fraction and χ is the bulk interaction parameter. Anionic polymerization techniques give direct control over molecular weight (i.e., N), which governs the domain size. Selecting the copolymer composition specifies the underlying structure upon ordering. For a symmetric or near-symmetric diblock in a neutral solvent (one that is equally attracted to both blocks), a lamellar microstructure will form when the system orders.[14]

Our investigations of concentrated macromolecular liquids are motivated by the fundamental issue of understanding polymer phase behavior in confined systems and the resulting influences on properties. We have chosen a polystyrene–polyisoprene diblock copolymer for these studies. The behavior of this system should differ inherently from that of tethered chains, as neither block of the PS–PI diblock adsorbs strongly on the confining mica surfaces. Another distinct difference between polymer brushes and this system is that, in order to introduce regular, long-range structure into the system, the concentration of the diblock in solvent must be many orders of magnitude higher than that of the polymer brush systems studied to date. As the surface forces apparatus has shown great utility in elucidating the structure–property relationships of a wide variety of structure-forming liquids, we expect that such measurements would be sensitive to differences in structure of a confined diblock copolymer liquid. Ultimately, we want to examine the complete structure–property relationships of this system as well as probe its surface interactions.

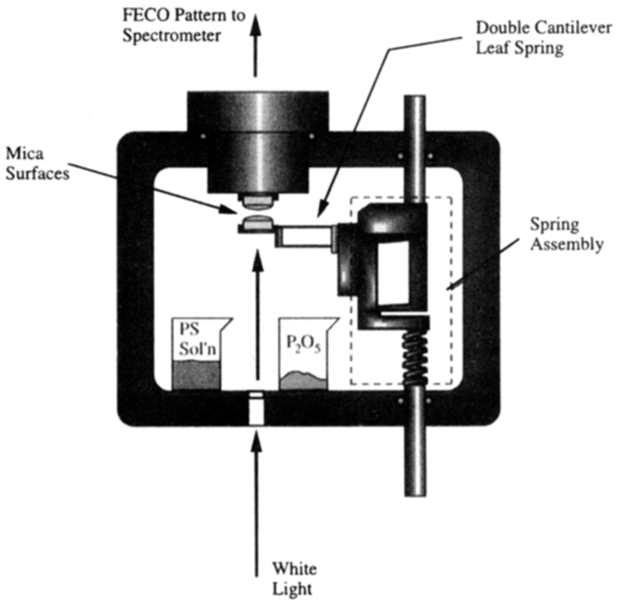

Figure 1. Schematic diagram of the Mark II surface forces apparatus. To perform the dynamic experiments, the mounting bracket of the double-cantilever leaf spring is replaced by a piezoelectric driver. Frictional force detection is performed at the upper surface by replacing the static upper surface mount with a differential capacitor head, on which the upper surface is mounted.

Experimental Section

Material. The block copolymer used in this experiment was anionically polymerized and characterization determined its molecular weight to be 21 000 with a polydispersity index of 1.04. The polymerization was carried out such that the block copolymer was symmetric ($f \approx 0.50$). We refer to this particular polymer as (10–10)K PS–PI, with the numbers referring to the molecular weights of each block in thousands. The mica used for the surface forces experiments was obtained from S&J Trading of New York. The ASTM V-2 Muscovite mica was cleaved to sheets 1–3 μm thick and areas of approximately 1 cm^2.

Sample Preparation. Spectroscopic-grade toluene was filtered through a 0.22-μm Millipore filter prior to use. The diblock solutions were made by dissolving the copolymer in toluene and allowing the samples to stand for 5–7 days before use. During this time, the samples were refrigerated to help minimize polyisoprene degradation. Solutions with weight fractions of diblock, w, of 0.10, 0.20, 0.30, 0.40, 0.55, and 0.66 were prepared.

Force Measurements. A Mark II surface forces apparatus similar to the one constructed by Israelachvili was used for the direct force measurements.[1,11] A schematic of this device is shown in Figure 1. The separation between the surfaces is controlled by the upper micrometer-driven shaft and lower micrometer-driven shaft. The motions of the lower shaft are reduced approximately 3 orders of magnitude by the spring assembly, and, through this, nanometer increments of distance control are possible. An optical technique using fringes of equal chromatic order (FECO) is used to measure the separation distance between the surfaces and the shape of the confining surfaces.[15] With this technique, the separation distance can be measured as accurately as 2–3 Å. As a result of this distance accuracy, normal force resolution as small as 10 μN is attainable. Forces are measured by monitoring the deflection of the double-cantilever spring. The difference between the known distance the lower micrometer-driven shaft was moved and the resultant motion of the lower surface, multiplied by the spring constant of the double-cantilever spring, yields the normal force. By normal, we refer to the mode in which the surfaces are moved normal to one another, i.e., compression and expansion.

To ensure that the measurements were taken at equilibrium and the measureed distance is accurate, it is necessary to take several precautions at different stages of the experiment. Before a force profile can be recorded, one must verify that the system is in thermal equilibrium. This is achieved by monitoring one of the FECO fringes for approximately 20 min. If the monitored fringe does not drift, then there is no expansion or contraction of the apparatus, and thermal equilibrium has been reached. Usually, 8–12 h were needed to achieve this condition. In all cases, the normal force experiments were conducted at a constant temperature of 32 °C, while the shearing experiments were performed at a constant temperature of 25 °C.

Relaxation of the confined liquids was observed by tracking the FECO fringes, which provides a direct measurement of how the separation distance between the two surfaces changes during a force profile measurement. For these studies, individual data points were not recorded until the surfaces exhibited no further motion following a change in surface separation. This often required 3–8 min. Finally, to ascertain that the FECO fringe tracked throughout the experiment was in fact the reference fringe, the surfaces were forced into high-pressure contact after all the force profiles had been recorded. This enabled verification that the correct fringe was used. This is essential due to the multiple fringes created by the multilayer interferometer formed by the surfaces and confined fluid. Greater detail on multilayer interferometry can be found in ref 15.

These experiments are performed by placing a droplet of the polymeric liquid between the surfaces. In order to equilibrate the osmotic pressure between the sample and the chamber of the surface forces apparatus, a solution of a nearly monodisperse polystyrene homopolymer in toluene was used in both types of experiments. A small vial of an osmotic pressure equilibration solution of the necessary composition was placed in the chamber of the surface forces apparatus. This measure is necessary to prevent evaporative losses from the sample. Several normal force experiments were checked for reproducibility over the course of 48 h or longer after the initial experiments were performed. In all cases, the position and level of the measured forces were unaltered, verifying that evaporative losses were prevented or negligible. A small vial of phosphorus pentoxide, which scavenges moisture, was also placed in the sealed chamber.

Adaptation of the surface forces to provide a means of investigating the dynamic behavior through shearing types of experiments has recently received much attention. To carry out dynamic experiments, the experimenter may choose to drive the confining surfaces either normal to one another[16,17] or parallel to one another.[18–20]

The shearing measurements are made using two special components to replace the upper and lower disk mounts. The lower surface is driven by a piezoelectric bimorph, and response detection is performed with a differential capacitor at the upper surface. Extremely parallel motions as small as 6 Å or as large as 15 μm may be imparted to the lower surface with response detection on the order of 10^{-3} mN possible. A Hewlett Packard 3325B function generator and SR530 lock-in amplifier by Sanford Research Systems are used for drive signal generation and response detection, respectively. The separation distance control and precision is unaltered from the original Mark II design. *A priori* calibration of the piezoelectric driver and differential capacitance head provides a means of converting the input voltage to amplitude and the response signal to a frictional force.

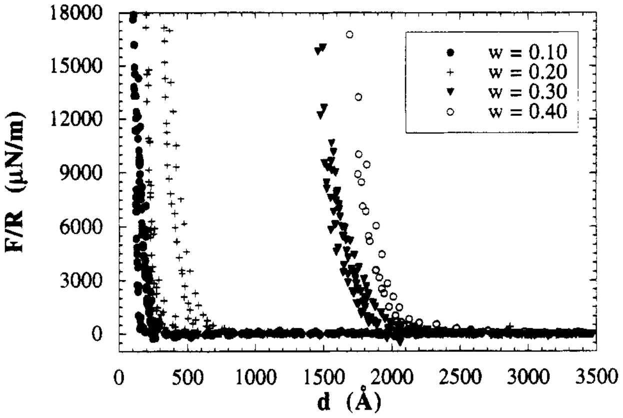

Figure 2. Intermolecular force versus distance between confining mica surfaces immersed in solutions of (10–10)K PS–PI in toluene at 32 °C. The weight fractions presented correspond to samples that on continuum (bulk) length scales have no long-range order.

The most critical design criteria rest in ensuring extremely parallel motion between the surfaces. Since the shearing modifications do not interfere with the optics of the system, we can monitor the movement of the surfaces normal to one another with the accuracy imparted by the interferometric technique as the surfaces slide parallel to each other. We find that the separation distance between the surfaces changes by less than 10 Å at total travel distances up to 10 μm. In our experiments, the maximum amplitude used was approximately 7 μm.

In the dynamic surface forces experiments, the drive signal was triangular ramp. This type of function gives rise to constant shear rate experiments. By adjusting the amplitude, frequency, and separation distance between the surfaces, the shear rate may be varied. For all of these experiments, the separation distance was set and several sweeps of frequency and amplitude were made in order to change the shear rate. After spanning several orders of magnitude in shear rate at a given separation distance, the distance between the surfaces was changed and the sweep runs were repeated.

Birefringence Measurements. Birefringence measurements were made by passing a horizontally polarized beam of light from a 15-mW He–Ne laser through the sample contained in an optical glass dynamic light scattering cell. The sample cell was contained in a toluene bath that was temperature regulated with a Endocal refrigerated circulating bath made by Neslab Instruments. The use of toluene ensured that the path entering to and exiting from the sample in the bath was isorefractive. The light exiting the sample was passed through a vertical polarizer and focused onto a photodetector. The output was measured with a voltmeter. The experiment consisted of increasing the bath temperature to increase the sample temperature and recording the resulting photodetector output. Additional information regarding birefringence experiments and their use in identifying the ODT of diblock copolymer solutions may be found in ref 21.

Results

Normal Force Results. Figure 2 shows the normal force profiles from the w = 0.10, 0.20, 0.30, and 0.40 solutions. As concentration, and therefore the order parameter, increases, the distance corresponding to the onset of monotonic repulsion increases. A marked increase in this force onset distance occurs when the weight fraction of diblock is increased from 0.20 to 0.30. If the diblock concentration is increased above w = 0.40, the force profiles unexpectedly shift to shorter separation distances, as shown in Figure 3. To identify the order–disorder transition of this polymer near the

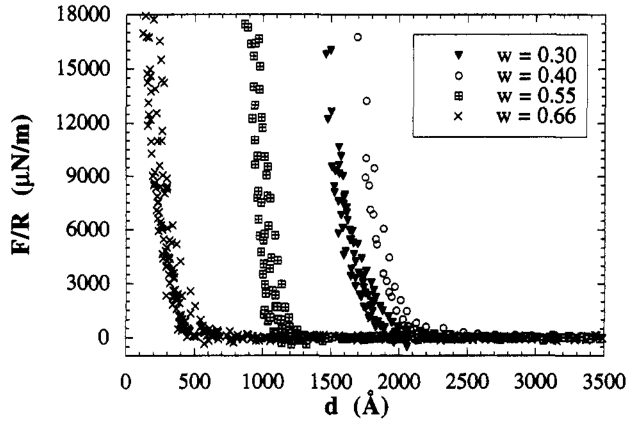

Figure 3. Intermolecular force versus distance between confining mica surfaces immersed in solutions of (10−10)K PS−PI in toluene at 32 °C. The weight fractions presented correspond to samples that are disordered, are strongly fluctuating ($w = 0.30$ and 0.40), or contain long-range-ordered structure brought about by surface-induced ordering ($w = 0.55$ and 0.66).

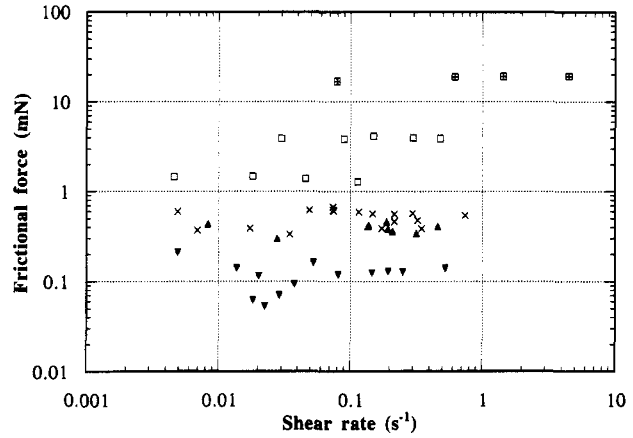

Figure 4. Frictional force versus shear rate for solutions of (10−10)K PS−PI in toluene confined between mica surfaces at 25 °C. The × symbols correspond to $w = 0.10$ specimens at normal force loads (NF) ≤ 2500 μN m^{-1}. Open squares represent data for $w = 0.30$ samples at NF ≤ 2500 μN m^{-1}, while the hatched squares denote $w = 0.30$ samples at NF > 2500 μN m^{-1}. The ▼ represent data for $w = 0.66$ specimens at NF ≤ 2500 μN m^{-1}, and the ▲ symbols correspond to $w = 0.66$ and NF > 2500 μN m^{-1}.

temperatures of the surface forces experiments, birefringence measurements[21] were conducted on samples of high concentrations. These measurements indicated that a solution of $w = 0.70$ diblock orders at a temperature of 33 ± 1 °C and a solution of $w = 0.66$ orders at a temperature of 22 ± 1 °C. Therefore, all of these force measurements on confined solutions were conducted at concentrations and temperatures corresponding to a disordered bulk state.

Shearing Results. Shearing surface forces experiments were conducted on samples of $w = 0.10$, 0.30, and 0.66. Figure 4 shows the results of these experiments plotted as frictional force versus shear rate. Each data point represents a signal-averaged response over several (more than four in all cases) cycles. The data taken at normal force loads of less than 2500 μN m^{-1} reflect that, over the shear rate range studied, the highest concentration tested ($w = 0.66$) produced the lowest frictional force while the intermediate concentration disordered sample ($w = 0.30$) exhibited the strongest resistance to flow. The shearing results reflect the same trend exhibited by the normal force results. Both the frictional forces and the range of repulsive normal forces increase with increasing concentration up to approximately $w = 0.50$ and then decrease as the degree of ordering strengthens. Another interesting feature arising from the shearing data is that, for any given diblock concentration, the frictional forces appear to be independent of the shear rate within the limits of our experimental error.

Discussion

We attribute the increase in the range of normal forces and the magnitude of the frictional forces as the solution concentration approaches approximately $w = 0.50$ and the subsequent reduction in the range and magnitude of the forces at higher concentrations to be reflective of the morphology of the confined liquid. We have used the amount of diblock in solution to govern the structure of the copolymer in the solvent. At very low concentrations the morphology of the liquid would be near-Gaussian coils. At concentrations above the ODT (or, conversely, temperatures below the order−disorder transition temperature), this diblock would form a lamellar microstructure. Between these two limiting regimes, as the volume fraction of diblock is increased and the ODT approached, the structure of the system becomes more complex.

While a mean-field picture is sufficient to describe the phase behavior well above and below the ODT, in the neighborhood of the ODT, the mean-field picture cannot account for local structural effects of the blocks. As the system approaches the ODT, microdomains rich in one block develop, with the junction points between the two different blocks becoming localized at the microdomain interfaces. While no long-range order exists, the overall character of the system is to segregate the two microdomains. The system remains weakly segregated, however, such that the block junctions are mobile and one component of the diblock may penetrate the microdomains of the other. Characterizing the local structure of the blocks and their spatial profile in this “weak segregation limit” (WSL) has been an area of much recent interest.

Bates and co-workers[22−24] have used rheology and neutron scattering to investigate the WSL behavior of a model polyolefin diblock copolymer melt. Both techniques verified the presence of composition fluctuations over a large temperature range (up to 50 °C) above the ODT. From small-angle neutron scattering (SANS) experiments they deduced the near-ODT morphology of their system. They concluded that the (equilibrium) instantaneous morphology resembled that of a spinodally decomposed binary mixture. In the ordered state, fluctuations lead to the development of defects and distortion of the lamellar order.[25]

Fredrickson and Helfand[26] applied the Brazovskii treatment for weak first-order phase transitions to Leibler's mean-field approach[27] in developing the first fluctuation theory for the ODT in block copolymers. This theory predicts that, for the lamellar morphology, the amplitude of the fluctuations in the composition pattern is of $O(N^{-1/6})$. For a disordered sample, these fluctuations increase in amplitude as the ODT is approached.[23,28] At the ODT, a weak first-order transition cuts off the growing fluctuations and the long-range-ordered structure forms.[26] Some fluctuation effects persist after the system has ordered, but as the order in the sample strengthens, those effects die out and a mean-field model will again become applicable. In the limit of

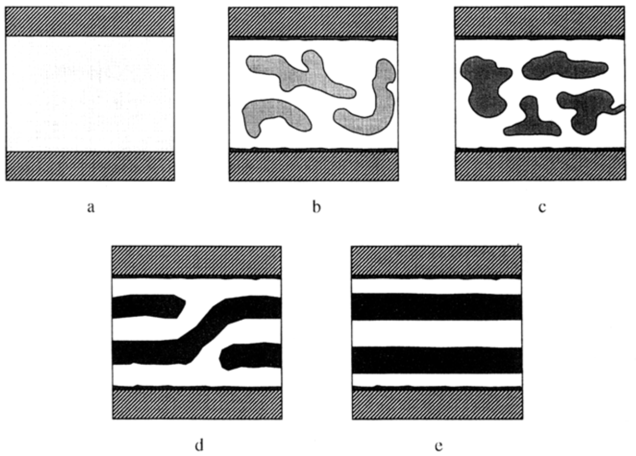

Figure 5. Proposed structures for (a) the low concentration, isotropic liquid state, (b and c) fluctuating disordered regimes approaching the ODT, and (d and e) microdomains pretransitionally ordered due to surface-induced ordering. In all cases, the solvent is not specifically depicted but taken as a uniform background.

infinite molecular weight, Leibler's mean-field behavior should be recovered.[27]

We suggest that our results can be explained by the presence of fluctuations and the phenomena of surface-induced ordering, as illustrated in Figure 5. As concentration increases, the disordered samples develop composition fluctuations of increasing amplitude and correlation length (Figure 5b,c). The associated composition gradients create an impediment to the movement of the block copolymer chains. In bulk (three-dimensional) specimens this is reflected in the low-frequency rheological properties as an increase in the complex shear modulus and shift to longer times of the onset to terminal behavior.[25] Locally, the response to an applied strain is inherently anisotropic. A maximum stress will be supported when the applied load is directed along the composition gradient, while the least resistance to deformation is obtained when the force is directed perpendicular to the gradient. Experiments with shear-aligned bulk lamellar specimens (below the ODT) corroborate this picture. In the disordered state the amount of cooperativity required to obtain flow will depend on the degree to which local structure is correlated in space. As the ODT is approached, the correlation length increases and stress relaxation depends on the cooperative rearrangement of a larger and larger volume of locally ordered material. This increase in spatial correlation is further reinforced by a growing amplitude in the local composition profile. We believe that the development of such fluctuations accounts for the increase in the separation distance at which monotonic repulsion is observed in the normal force profiles as w increases from 0.10 to 0.30 and 0.40. Furthermore, that distance associated with these force profiles provides a direct measure of the fluctuation correlation length (Figure 2). This interpretation is also consistent with the observed increase in frictional force at $w = 0.30$ (Figure 4).

We believe that the reduction in normal forces at the higher weight fractions ($w = 0.55$ and $w = 0.66$) occurs due to surface-induced ordering. Birefringence experiments indicate that, at the temperatures at which the normal force measurements were conducted, ordering of the bulk state does not occur until the weight fraction of diblock copolymer equals or exceeds $w = 0.70$. Our speculation is that, at the highest concentrations tested in the surface forces apparatus, the confining surfaces, which impose a nonhomogeneous field on the intervening liquid, coupled with a thin, template layer of copolymer residing at the surface,[29] cause the short-range order present in the system to build across the intervening macromolecular liquid, and a regularly ordered structure forms. The net result is pretransitional ordering of the sample.

The effect of surface-induced ordering in diblock copolymer systems has been studied theoretically by Binder,[30] Fredrickson,[31] and Harris.[32] Despite the different mathematical approaches to studying this phenomenon, each concludes that confining surfaces that have an affinity for one block of a diblock copolymer lead to regular ordering at conditions that in the bulk state would otherwise correspond to a disordered state. This ordering arises from a reduction in the free energy of the system due to the presence of the confining surfaces. Experimentally, some of the earliest surface forces experiments on simple, isotropic liquids evidenced quasi-discrete layering as a result of the confinement of molecularly smooth surfaces.[1,4] Thin film experiments on bulk diblock copolymers[28,33] have shown that surfaces can produce damped oscillatory variations in concentration propagating away from the interface, resulting in the penetration of order in the film to various degrees somewhat below the bulk ODT.

Also, based on a significant body of theoretical and experimental results, we believe that the lamellae tend to lie parallel to the confining surfaces.[28,34] The $w = 0.66$ sample exhibits the highest degree of ordering because of its proximity to the bulk ODT and, as a result of the lamellae stacking, offers little resistance to being removed from between the confining surfaces as they are brought together. There is no penalty for changing the number of confined lamellae stacked between the surfaces until the final periodic repeat structures that interact with each surface are reached. This is supported by the position at which the normal force profiles of the $w = 0.66$ specimen begin to show repulsion. The $w = 0.55$ sample does not shift to as small of a separation distance primarily for two reasons: although this sample is ordered, it is not strongly ordered, and fluctuations still should be present in this sample. Additionally, because the ordering in this sample is not as strong as the $w = 0.66$ liquid, folding and layering imperfections in the lamellae arising from the delicate entropy–enthalpy balance that drive the weak first-order transition are present (Figure 5d). These imperfections do not allow the strict regular order exhibited by more concentrated solutions. We believe these effects explain the location and breadth of the $w = 0.55$ force profiles relative to the more concentrated $w = 0.66$ sample and the strongly fluctuating, disordered ($w = 0.30$ and 0.40) samples.

These fluctuation and surface-induced ordering effects also explain the pattern of behavior seen in the shearing experiments. We have taken the solvent molecules as forming a consistent, uniform background for the macromolecular system. As a result of the copolymer composition, lamellae should form in the ordered state. Lamellae stacking parallel to the walls slide relatively freely over each other, thereby giving rise to low frictional forces. The $w = 0.10$ sample, while neither ordered nor fluctuating, exhibits a slightly higher frictional force due to an overlapped configuration of the polymer chains. The $w = 0.30$ and 0.40 liquids, which are disordered samples, show much higher frictional forces due to the interference created by the large-amplitude composition fluctuations.

In the dynamic measurements we have differentiated between data points taken at loads less than and greater than 2500 μN m^{-1} in an attempt to encapsulate in a simple manner the effect of separation distance, and, therefore, normal force, on these measurements. The system we have studied exhibits shear forces that depend strongly on the separation distance in a way we cannot explain completely. For example, the two distinct stratifications (with respect to frictional force) of the $w = 0.30$ data at normal forces less than 2500 μN m^{-1} correspond to two distinct separation distances, with the lower frictional forces occurring at a lower normal force (or, equivalently, at a greater distance). We do not expect that this simplification accounts for all of the complexity associated with these measurements on this diblock copolymer liquid; however, it provides a basis for comparison.

Figure 5 depicts the proposed structure of the macromolecular liquid confined between the mica surfaces at various concentrations of diblock in solution. In this figure, the solvent is taken as a uniform background, and greater gray-scale contrast in the disordered structures indicates composition fluctuations of increasing amplitude. At low concentrations the structure corresponds to an isotropic, disordered liquid as shown in Figure 5a. When the concentration of diblock in solution is increased and the ODT is approached, large-amplitude composition fluctuations grow into the confined sample (Figure 5b,c). At high enough weight fractions, although disordered in the bulk state, confinement on molecular levels causes surface-induced ordering into lamellar microdomains (Figure 5d,e). These ordered lamellar microdomains formed at sufficiently high concentrations are separated by defect-rich grain boundaries. For both the isotropic and lamellar structures, the polymeric domains are well-defined, and as a result the exhibited intermolecular normal force and frictional force are lower than those exhibited by the intermediate concentration samples experiencing composition fluctuations. Although these surface forces measurements do not provide direct information as to which polymer block has a higher affinity for the mica surfaces, the structures depicted in Figure 5 would not change if, for example, the PS chains were assigned as the white areas instead of the shaded domains since the polymer is symmetric.

Conclusions

We have demonstrated that direct force measurements with a surface forces apparatus operated in normal and shearing modes provide an avenue for investigating structural behavior for an essentially nonadsorbing macromolecular liquid confined on a noncontinuum length scale. We suggest that a non-mean-field description of the phase behavior, coupled with the effect of surface-induced ordering, encapsulates the behaviors exhibited in both the normal force measurements and shearing experiments. In each case, the fluctuating, disordered liquid exhibits stronger resistance to flow than either the isotropic or pretransitionally ordered morphologies. Pretransitional ordering in the vicinity of the ODT appears to result from confinement. These surface forces experiments provide unique characterization of these soft materials.

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