Confinement-induced miscibility in polymer blends

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The use of polymer thin films in technology is increasingly widespread—for example, as protective or lithographic surface coatings, or as active (electronic or optical) elements in device architectures. But it is difficult to generate films of polymer mixtures with homogeneous surface properties, because of the tendency of the polymers to phase-separate1–2. Copolymer compatibilizers can induce miscibility in polymer blends, but only with chemical components that are either close to a critical point in the phase diagram or which have an attractive interaction between them3,4. Instead of manipulating the chemical composition of the polymers, we approach this problem in the following stages. First, we perform a series of experiments on thin film polymer blends. Then, we proceed to test the theoretical predictions by performing a series of experiments on thin film polymer blends.

We use a numerical self-consistent field (SCF) model based on the method developed by Scheutjens and Fleer4. The SCF method studies polymeric phase behaviour by combining markovian statistics with a mean-field approximation. In this model, the free energy of the system is:

\[ F = k_{\text{B}} T \ln \Omega + \sum \chi \psi(r)(1 - \phi_i(r)) \]  

where the first term represents the entropy of the system, and the second term represents the enthalpy of the system. Here \( k \) is Boltzmann’s constant, \( \Omega \) is the number of conformations possible, \( \chi \) is the Flory–Huggins parameter that represents the various monomer–monomer interaction energies and \( \phi_i(r) \) is the concentration of species \( i \) at position \( r \). The aim of the calculation is to determine a concentration profile that minimizes the free energy of the system.

We focus on linear symmetric diblock copolymers, as these copolymers have been shown to pack more efficiently at the interface than comb, star or random copolymers5. Therefore, if we understand how to retard micelle formation in diblock copolymers, these copolymers will be the most efficient at reducing the interfacial tension between the polymer phases. In our model, we assume that the micelles formed are spherical, because studies have shown that due to kinetic effects, spherical micelles are the primary micelle structure over a wide range of copolymer concentrations.

In Fig. 1a we plot the critical micelle concentration (c.m.c.; the concentration at which micelles first appear in the system) for two different diblock copolymers as a function of the degree of...
confinement. We see that large changes in the c.m.c. only happen at high degrees of confinement. Initially, at small degrees of confinement, the micelle reacts by undergoing a slight decrease in its size (Fig. 1b). This change in size, however, is not large enough to affect the free energy of micelle formation. As we increase the confinement further, the micelle gets smaller and the entropic losses that occur with the packing of linear diblock copolymers into smaller and smaller spheres starts increasing rapidly. Consequently, the formation of micelles becomes energetically unfavourable, and this shows up in a large increase in the c.m.c. of the system.

The length scale at which confinement changes the behaviour of the system is approximately twice the radius of the bulk micelle (Fig. 1a). It is important to note, however, that even though the length scale appears related to the bulk micelle size, at this point the size of the micelle is roughly half the size of the original bulk micelle. After this point, the c.m.c. of the system increases very rapidly and consequently so does the chemical potential of the micelle. After this point, the c.m.c. of the system increases very rapidly and consequently so does the chemical potential of the micelle. At high enough concentrations of copolymer, this migration should result in a vanishing interfacial tension and in the formation of a microemulsion phase.

To test the theoretical prediction we chose an experimental system consisting of two well characterized monodisperse (that is, the polydispersity index is < 1.1) polymers, polystyrene (PS) and polymethylmethacrylate (PMMA). The molecular masses of PS and PMMA were 200,000 and 296,000 daltons, respectively. We chose this system because these homopolymer pairs are highly incompatible (the \( \chi \) parameter between the homopolymers is \( \sim 0.04 \)) and in this strongly segregated system, the formation of a microemulsion has never been observed.\(^6^{10}\). The diblock used in this study was a 37,000–46,000-dalton deuterated PS–dPS–PMMA copolymer. Previous studies have established that in bulk systems, this copolymer forms spherical micelles in the PS phase.\(^14\) Using an analytical expression derived by Semenov, we estimated the diameter of these micelles to be 560 Å. All the samples were prepared in the following manner. First, on a cleaned Si substrate we spun-cast a thick layer of PMMA (>570 Å). On it, we floated a layer that contained PS and 30% copolymer dPS–PMMA—a concentration which is much larger than the c.m.c. of the diblock.\(^14\) We control the degree of confinement in our system by controlling the thickness of the top PS layer. To reach equilibrium, all the samples were annealed in a vacuum of \( 10^{-7} \) torr at 180°C for times ranging from 24 hours to a week.

In Fig. 2, we show scanning force microscopy (SFM) images of the bilayer samples. For thick PS layers (>900 Å), we can see the micelles that remain after the dissolution of the PS phase on the surface of the PMMA layer (Fig. 2a). When the PS layer thickness was then gradually decreased to less than the size of the bulk micelle diameter (<560 Å), the point where the theory predicts a large change in the c.m.c. of the system, the two homopolymers completely mixed (Fig. 2c). From Fig. 2d we can see that the resulting structure is a microemulsion with columnar domains that extend through the entire film. This maze-like configuration has a characteristic period which corresponds to a domain spacing of 600 nm.

To make sure that we were not influencing the morphology of the system by our washing procedure, we also performed near edge X-ray adsorption fine structure (NEXAFS) microscopy scans of the thin-film blend samples. NEXAFS microscopy is a technique by which we can obtain two-dimensional composition profiles of thin
films with a spatial resolution of 40 nm without any further sample treatment\(^1\). For films where the thickness of the PS layer was 1,100 Å (Fig. 3a and b), spherical micelles can be clearly seen in the system. When the PS layer is decreased to 380 Å (below the diameter of the bulk micelle), a microemulsion phase with a well-defined wavelength is observed (Fig. 3c and d). The height of each of the domains in the pattern is approximately equal to the initial thickness of the sample, indicating that the structure extends all the way to the substrate in agreement with the SFM results. In the total density profile, which yields the same information as SFM topography, only a slight roughening of the surface is observed. This is in sharp contrast to observations of bilayers of thin PS on PMMA\(^14\) (without compatibilizer), where the PS formed droplets (with well-defined contact angles) on the PMMA, rather than wetting it. Thus we believe that what we are observing here is the formation of a true microemulsion phase, and not a phase-separated system. We note that the NEXAFS microscopy will allow us to monitor the dynamics of microemulsion formation, and work on this is in progress.

To confirm the location of the diblock copolymer at the interface between the PS–PMMA domains, we washed the sample that formed the microemulsion with cyclohexane and scanned it using the lateral force mode of the SFM. The regions with higher friction contrast are located at the edges of the PMMA domains (Fig. 4). These are due to the PS block of the diblock copolymer, unlike the PS homopolymer, does not readily dissolve in cyclohexane.

As our approach does not restrict the chemical nature of the polymers, it should be able to produce complete mixing in any system in which the formation of micelles limits the miscibility of the blend. We therefore expect that this method will have a significant effect on any technological process that relies on ultra-thin polymer coatings, such as photolithographic printing and magnetic-disk coatings, as our technique produces films that are perfectly flat and completely mixed.

Received 12 February; accepted 20 April 1999.