

SELF-ASSEMBLY BY PHASE SEPARATION IN POLYMER THIN FILMS

by

A. Karim, J.F. Douglas, L.P. Sung, and B.D. Ermi

National Institute of Standards and Technology
Gaithersburg, MD 20899 USA

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Self-assembly by Phase Separation in Polymer Thin Films

The prediction of thin polymer film properties is a recurrent problem in manufacturing. Estimates of the properties of these films from bulk material properties and from simplified models that ignore the detailed nature of the film morphology can be inaccurate. This difficulty complicates manufacturing design in the electronics industry, for example, where thin polymer films are utilized in the fabrication of semiconductor devices. Moreover, many commercially important polymer films, such as those found in paints and other coatings, are mixtures of polymers (blends) and other suspended matter that may be homogeneously or heterogeneously mixed. Making the best use of these mixtures requires an understanding of factors that control film morphology and the state of particle dispersion. This technologically important problem of optimizing thin film properties motivates fundamental scientific studies on how the film thickness influences the dynamics of demixing and the morphology of thin polymer blend films.

It is usually difficult to form thermodynamically stable polymer blends of high molecular weight molecules, since the entropy of mixing for these systems is rendered small due to chain connectivity (Flory 1971) (see *Polymer Mixtures, Thermodynamics of, Polymer Blends: Structure and Properties, Polymer Blends: Overview of Industrially Significant Blends*). In general, the state of mixing of a blend film is dictated by temperature, film thickness, and the chemical nature of the boundaries and polymers. A change in temperature, from the homogeneously mixed to an unstable temperature regime, initiates phase separation where the two blend components spontaneously demix from their initially homogeneous state. The heterogeneity of the films accompanying phase separation generally leads to changes in the film properties.

Observations on blend film phase separation can be roughly categorized into *thick* (having a morphology similar to bulk blends except for “skin” regions near the boundaries of the film) and *thin* (thickness on the order of a micron where the perturbation of the phase separation morphology becomes appreciable). There is also an “ultrathin” regime of film thickness where the films are sufficiently thin so that they behave quasi two-dimensionally (See discussion below). In contrast to the thick films, experiments on thin blend films are typically characterized by the formation of alternating layers rich in the blend components (Jones *et al.* 1991, Krausch *et al.* 1994, 1993). This layering is initiated by a preferential attraction for one of the polymer components to the surface, arising from a difference in relative affinities of the polymers for the substrate (see *Polymer Surfaces: Segregation*). This leads to a segregation of the favored polymer component to near the surface. The other component then forms a layer

next to the first layer and the process continues, so that an alternating composition pattern develops (similar in form to a Neopolitan layer cake), where the penetration depth of this layering depends on the surface interaction and quench depth. In the case where one polymer is enriched at both film boundaries, the layered structure can be suppressed (Sung *et al.* 1996) if the film thickness is smaller than the initial scale of the bulk phase separation pattern (“spinodal wavelength”). Phase separation then occurs within the plane for films having a thickness less than a characteristic scale L_c , which is typically on the order of 100–200nm (Sung *et al.* 1996, Ermi *et al.* 1997, 1998, Gruell *et al.* submitted). The present article focuses on ultrathin blend film phase separation.

Polymer mixtures can phase separate either upon raising or lowering temperature. Phase separation upon heating is termed “lower critical solution phase separation,” while phase separation upon cooling is termed “upper critical solution phase separation”. Figure 1 schematically illustrates these types of phase boundaries encountered in the discussion below. We consider a blend of deuterated polystyrene (dPS) and polybutadiene (PB) ($M_w = 1000$ ($M_w/M_n = 1.13$) and 5300 ($M_w/M_n = 1.07$), respectively) which has an upper critical solution type phase boundary (bulk critical temperature and critical polystyrene (mass fraction) concentration of 51°C and 0.7, respectively). The blend dPS and polyvinylmethylether (PVME) ($M_w = 5.67 \times 10^5$ ($M_w/M_n = 1.3$) and 2.35×10^5 ($M_w/M_n = 1.9$), respectively) to illustrate the lower critical solution type of phase boundary (bulk critical temperature and critical polystyrene (mass fraction) concentrations of $\sim 145^\circ\text{C}$ and ~ 0.2 , respectively). (According to ISO 3-8, the term “molecular weight” has been replaced with “relative molecular mass”, M_r . The conventional notation, rather than the ISO notation, has been employed in the present article.) Before describing our measurement, we briefly review some general aspects of bulk phase separation.

The phase separation process starts by the growth of the enrichment of local composition fluctuations toward the equilibrium concentrations of the coexisting phases defined by the phase diagram (see Fig. 1), but there is little growth in the spatial scale of the composition fluctuations in the early stage of phase separation. The scale of the fluctuations in this regime (spinodal wavelength) is of the order of the equilibrium interfacial width of the coexisting phases at equilibrium. For near-critical composition mixtures, the phase separation morphology is bicontinuous, i.e., forming an interpenetrating structure in which each phase forms a continuous connecting structure spanning the material.

The geometry of this spinodal phase separation pattern does not change in this intermediate stage of phase separation, but the spatial scale of the pattern grows according to a power law in time. Figure 2(a) illustrates the geometry of the intermediate stage

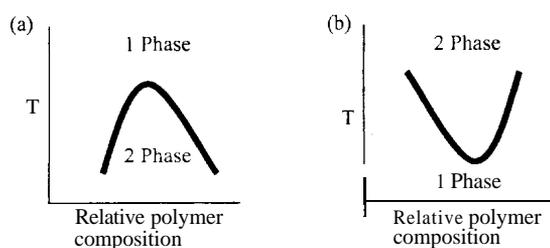


Figure 1
Schematic phase boundaries of polymer blends. (a) Phase separation upon cooling and (b) Phase separation upon heating. The lines show the locus of coexisting compositions upon phase separation.

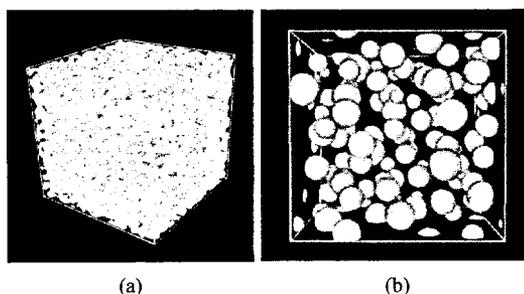


Figure 2
Simulated phase separation in a blend. (a) Spinodal phase separation pattern for a near critical composition blend. (b) Off-critical phase separation pattern in blend. Images were obtained by lattice-Boltzmann simulations (Martys and Douglas 2001).

morphology for a fluid mixture having a near-critical composition (50/50 relative volume fraction mixture). This image was obtained from a lattice Boltzmann simulation of phase separation (Martys and Douglas 2001). The fluid nature of the film becomes important in the final late stage of phase separation where thread-like structures, forming the spinodal pattern, break up into droplets through a capillary instability (Siggia 1979). This stage is dominated by appreciable fluid flow or *hydrodynamic* effects that increase the exponent describing the rate of pattern coarsening.

It is no longer possible for the phase separation pattern to remain connected when the composition is far from critical and droplets form, rather than a spinodal pattern. Figure 2(b) shows a lattice Boltzmann simulation of the resulting droplet morphology that forms in off-critical blends, corresponding to a 10/90 relative volume fraction of the fluid components (Martys and Douglas 2001). We next consider the appearance of phase separation in ultrathin blend films using optical microscopy (OM).

An ultrathin film (Sung *et al.* 1996) (thickness of 20 nm) of a near critical composition dPS/PB blend solution was cast from a toluene solution onto an acid

cleaned Si wafer and the evolution of phase separation morphology imaged in time (Fig. 3). The phase separation pattern has a strong resemblance to simulated phase separations in two-dimensions (Wu *et al.* 1995). (See Fig. 2(a) for the three-dimensional counterpart.) For thicker films (Sung *et al.* 1996) ($L = 100$ nm), the kinetics of phase separation is similar to that inferred from neutron scattering measurements on bulk blends, but we observe a different kinetics in thin film shown in Fig. 3.

The power law exponent describing the rate of coarsening of late stage phase separation is closer to $1/2$ compared to the value of 1 normally observed in bulk and thick film measurements (Sung *et al.* 1996, Wu *et al.* 1995, San Miguel *et al.* 1985). This finding agrees with earlier theoretical predictions (San Miguel *et al.* 1985) and simulations (Wu *et al.* 1995) of two-dimensional fluid phase separation. This seems to indicate that these very thin films begin to exhibit hydrodynamic properties of two-dimensional fluids so that the films are quasi-two dimensional in this sense (Sung *et al.* 1996).

The physical origin of the contrast in the OM images of ultrathin film phase separation is not clear from Fig. 3. Slawcki (1995) and Karim *et al.* (1998) first performed atomic force microscopy (AFM), neutron and x-ray reflectivity studies that showed that this contrast arises from height undulations in these films. The early measurements showed that AFM is particularly powerful for studying this type of surface pattern formation and Ermi *et al.* (1997, 1998) applied the method to the investigation of the kinetics of ultrathin blend film phase separation in real space. Figure 4 shows representative AFM images of a dPS/PVME blend film having a thickness of approximately 100 nm for a range of relative polymer compositions. The upper figure corresponds to a 55/45 relative dPS/PVME mass fraction, the middle figure is near the critical composition 35/65 and the bottom film corresponds to a 10/90 relative dPS/PVME composition.

The films were prepared by spin-casting the polymer solution (toluene solvent) on an HF etched silicon wafer and annealing for 40 min at 160°C . The films were then quenched to room temperature that freezes them due to the relatively high glass transition temperature of dPS. The hole, spinodal, and bump surface patterns reflect the surface tension variations within the film that accompany phase separation, where the hole and bump features correspond to a minority phase having a lower and higher surface tension, respectively (Sung *et al.* 1996, Ermi *et al.* 1997, 1998). This interpretation is confirmed by experiments where the temperature was reduced into the one phase region (115°C), but still well above the glass transition temperature of the blend (Ermi *et al.* 1997, 1998). The film returns to a smooth form as the film becomes homogeneous.

The conceptual model of ultrathin film phase

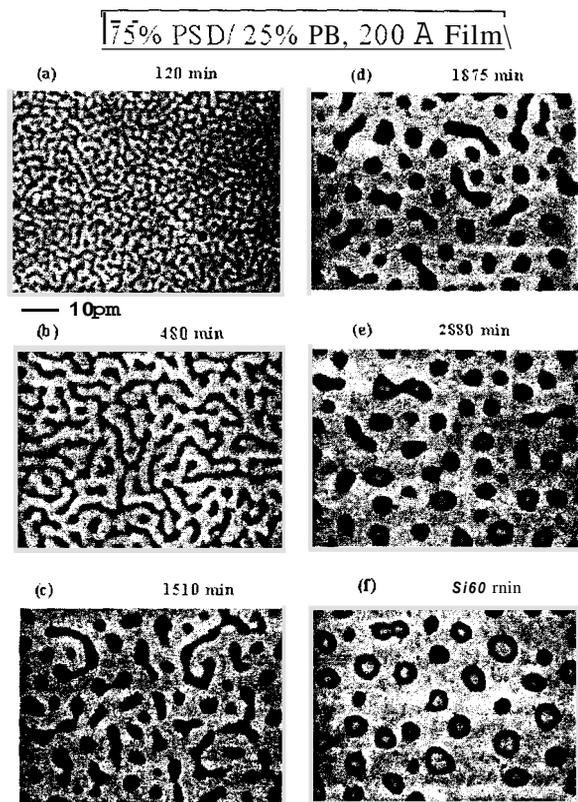


Figure 3

Optical micrograph of an ultrathin (20 nm) film (Sung *et al.* 1996) of polystyrene and poly(vinyl-methyl ether) at an intermediate stage of phase separation. The form of this pattern appears similar in time over an appreciable time scale, but the size of the pattern features grows steadily with time. This top view projection of the spinodal pattern does not distinguish between capillary-like or ribbon-like spinodal patterns. These ribbon-like fluid patterns break up into droplets of one of the components dispersed in the other phase depending on the relative viscosities, concentrations of the polymer components of the blend and film thickness and other factors which are not entirely known. The variations in darkness in the micrograph reflect height variations in the phase separated film thickness (see Fig. 4). The PS/PVME blend phase separates upon heating.

separation described above requires that a morphological transition takes place from a layered to an in-plane phase separation with decreasing film thickness. (We estimate the critical thickness, L_c , at which this occurs to be comparable to the spinodal wavelength, on the order of 100–200 nm, but this scale may be affected by the surface interactions.) Figure 5 shows a 200 nm dPS/PB blend film under the same conditions (temperature, surface preparation) as the 20 nm film shown in Fig. 2. This film remains smooth and featureless over 24 h, the timescale of the measure-

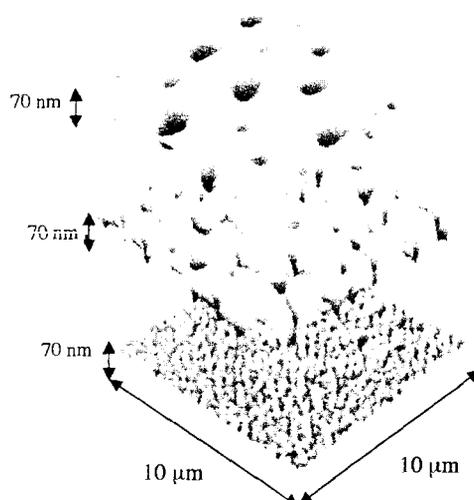


Figure 4

Atomic force microscopy image of an ultrathin film (100 nm) of polystyrene and poly(vinylmethylether) at a transition stage between intermediate and late-stage phase separation (Ermi *et al.* 1997, 1998). Variations of the interfacial tension within the phase separating layer cause the surface to buckle and the phase separation layer may then be easily followed by optical microscopy (Sung *et al.* 1996). This surface buckling has a similar origin to Bernard-Marangoni patterns formed at the free surface of films heated from below where the temperature gradient causes the variations of the surface tension within the layer that cause surface buckling and pattern formation.

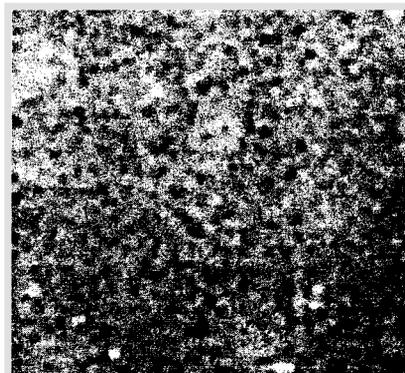


Figure 5

Optical microscopy (Sung *et al.* 1996) image of a dPS/PB film above the critical thickness (L_c). The film surface is smooth due to the formation of layers within the film (surface directed spinodal decomposition). Image width = 100 μm

ments. This transition is attributed (Sung *et al.* 1996, Ermi *et al.* 1997, 1998, Gruell *et al.* submitted) to a change from in-plane phase separation to a layering (“surface directed”) phase separation where the

smooth film is identified with the layered film geometry. More recent neutron scattering measurements on dPB/PI blends by Gruell *et al.* provide further support for such a transition between in-plane to transverse layering phase separation with increasing film thickness.

The measurements described here illustrate some of the changes in phase separation morphology occurring in thin polymer blend films. The changes in morphology are especially large when the films are thinner than the scale of the bulk material interfacial profile width. Under these circumstances, phase separation occurs within the plane of the film. Notably, the observation of in-plane phase separation requires that one of the components segregate preferentially to both boundaries. (The film stratifies into a bilayer if one of the components of the blend segregates to the air and the other to the substrate surface.) Optical and atomic force microscopy provide unique opportunities for studying ultrathin film phase separation in real space.

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A. Karim, J. F. Douglas, L. P. Sung, and B. D. Ermi

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