

Early-Stage Compositional Segregation in Polymer Blend Films

Wetting plays an important role in diverse applications ranging from insecticide sprays to detergency. This interest, in part, has motivated a great deal of fundamental research involving the spreading (wetting) of a liquid on a solid surface. Polymer blends are of great commercial importance and therefore their thermodynamic and phase separation behaviors have been widely studied.

The structure and properties of thin blend films are governed by the interplay between phase separation and surface segregation driven by polymer-surface interactions. The nature of the segregation depends on whether the mixture forms a stable one-phase fluid or phase-separates [1, 2]. In the former case, the surface-enrichment-layer (SEL) grows and stabilizes to an equilibrium value. In the latter case the initially formed SEL breaks into droplets for partial wetting and grows unsteadily for complete wetting [1]. The late stage evolution of the surface enrichment layers thus exhibits “non-universal” growth laws, depending on the phase stability, wetting characteristics of the blend, confinement, as well as on the details of the polymer-surface interaction potential [2]. The universality of surface segregation at the early-stage, however, has not been explored, partly because the compositional changes are normally rapid [3, 4]. We therefore designed a measurement that can access the short time and small length-scale surface-enrichment regime.

A critical blend film near the glass transition of the polymers is utilized so that the chain dynamics are greatly slowed down even under thermodynamically strong segregation conditions. The polymers are deuterated poly(methyl methacrylate) (dPMMA) and poly(styrene-*ran*-acrylonitrile) (SAN). This polymer blend has a lower critical solution temperature (LCST) below T_g as revealed by small-angle neutron scattering measurements. A 445 Å film of dPMMA/SAN (50/50 by mass) was obtained by spin-casting from a common solution. After drying at a temperature slightly below T_g , the films were annealed in a vacuum oven at (130 ± 0.1) °C for various times ranging from 1 min to 36 h. After drying and after each step of annealing, the film was measured using neutron reflectivity

(NR). An atomic force microscopy study indicated that the film roughness was below 6 Å throughout the measurement.

Figure 1 shows NR spectra after several annealing intervals. The spectra were analyzed using a model-fitting scheme. The best fits are shown as the solid curves, and their corresponding compositional profiles are shown in Fig. 2. The inset of Fig. 2 shows the evolution of the dPMMA volume fraction in the depletion zone (ϕ_d) and at the surface (ϕ_s). The former decreases monotonically, suggesting that equilibrium has not been achieved, while the non-monotonic variation of the latter is due to the surface relaxation at the initial time.

The surface excess, $z^* = \int [\phi(x) - \phi_d] dx$, is shown in Fig. 3, and can be fit to a power law $t^{0.41 \pm 0.01}$ for early times (solid line), and a stretched exponential form for the entire time (dashed curve). The latter gives $z^*(\infty) = 72$ Å at the saturation. z^* starts to deviate from the power-law behavior at about 9 h (indicated by the arrow in Fig. 3) corresponding to $z^* = 40$ Å and $\xi_s = 57$ Å, where ξ_s is the surface correlation length characterizing the decay of the surface enrichment composition. These crossover scales in the kinetics are comparable to the bulk correlation length $\xi_b \approx 60$ Å, suggesting a transient saturation. After that, the SEL will grow unsteadily, entering the later stage of the wetting layer growth [4].

The inset of Fig. 3 shows that ξ_s nearly follows a power law of $t^{0.25 \pm 0.01}$, except for initial times. Note that

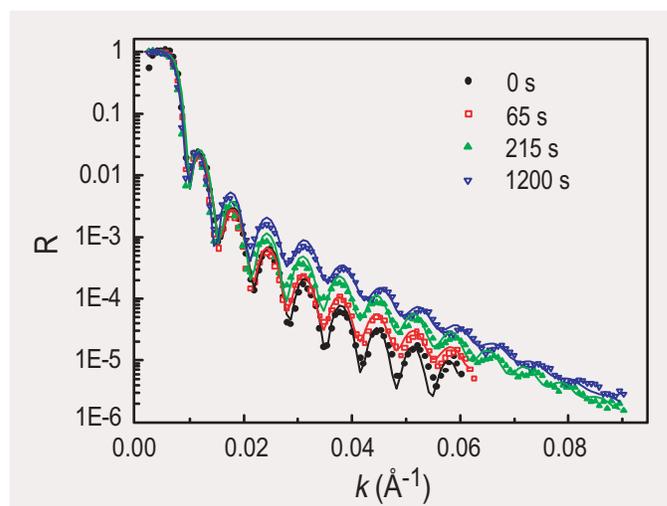


Fig. 1. Selected neutron reflectivity spectra after various times at 130 °C.

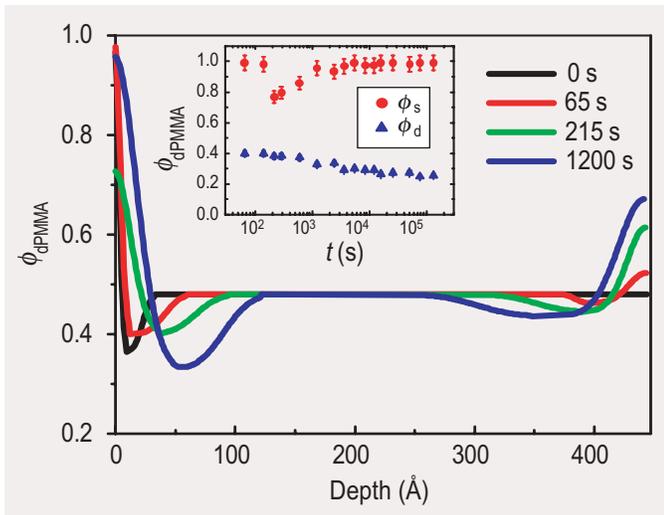


Fig. 2. ϕ_{dPMMA} profiles that give the best fit. The inset shows the evolution of surface composition, ϕ_s (circles) and depletion layer composition, ϕ_d (triangles).

right after drying, $z^*(0) = 4 \text{ \AA}$, indicating a segmental scale of saturation from processing the film (spin-casting and drying). Thus, the initial “anomaly” of ϕ_s and ξ_s may reflect the relaxation of the highly non-equilibrium compositional profiles. While most of the previous work focused on the kinetics after the formation of the initial layer on the order of the correlation length, the transient early-stage of the SEL has received little attention. The interpretation of the apparent power law growth will thus require further investigation.

In summary, during the early stage of surface segregation, enrichment at a monomer length-scale occurs first, followed by a segregation layer that grows to the order of the bulk correlation length, ξ_b , which coincides with the radius of gyration of polymers deep in the two-phase regime. Thus, the two observed distinct surface saturation states correspond to the characteristic scales of macromolecules. However, at near criticality, previous studies suggest a large discrepancy between ξ_s and ξ_b , pointing to the need to consider three length scales: that of the monomer, the molecular size, and the size of compositional fluctuations. The extent of universality in the early stage growth kinetics therefore needs further investigation. The present study is the first to quantitatively examine this important phenomenon.

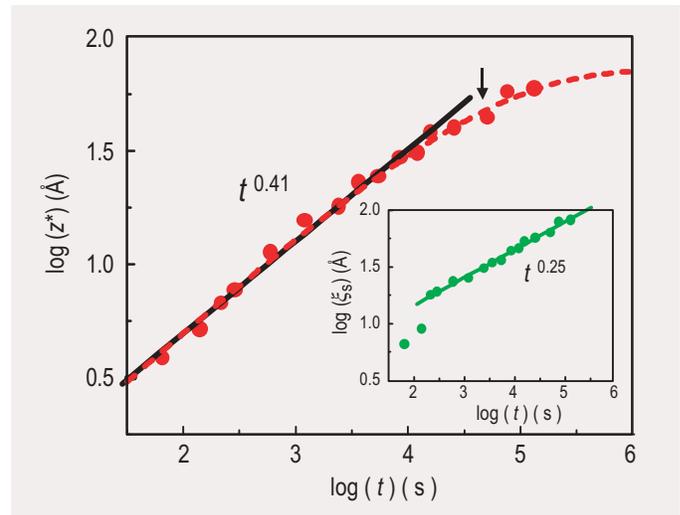


Fig. 3. z^* with a power-law fit (solid line), $t^{0.41}$, and a stretched exponential function (dashed curve). The arrow denotes a $z^* \approx 40 \text{ \AA}$ and the transition to slower growth. The inset shows the surface correlation length.

References:

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