Phase Separation in Thin Films of Polymer Blends: The Influence of Symmetric Boundary Conditions

MICHAEL WENDLANDT,* TOBIAS KERLE, MARCUS HEUBERGER, JACOB KLEIN**

Department of Materials and Interfaces, Weizmann Institute of Science, Rehovot 76100, Israel

Received 23 June 1999; revised 17 December 1999; accepted 21 December 1999

ABSTRACT: Using nuclear reaction analysis composition-depth profiling, we investigate the influence of symmetric/asymmetric confining walls on the equilibrium configuration of thin films of phase-separated polymer blends. Depth profiles of samples annealed under symmetric boundary conditions show a laterally averaged concentration, while samples confined by nonsymmetric walls show (as in earlier studies) clear separation into two thin layers of coexisting phases. This suggests that for phase separation under symmetric boundary conditions the interface between the two phases is orthogonal to the sample plane, in line with recent theoretical discussion. © 2000 John Wiley & Sons, Inc. J Polym Sci B: Polym Phys 38: 831–837, 2000

Keywords: polymer melts; solubility, segregation, and mixing; phase separation, fluid surfaces, and fluid interfaces; confined geometries; wetting

INTRODUCTION

Interfacial properties of thin polymeric films have technological importance for various applications in material science, for example, adhesive properties, lubrication, or coatings; at the same time, understanding the interplay between bulk and surface properties found in films of polymer mixtures poses an interesting scientific challenge. There is an extensive literature on surface enrichment and phase separation in thin films of binary polymer mixtures, which has been recently reviewed.[1] Experimental studies[2–5] of the equilibrium configuration in thin films of partially miscible polymer mixtures, especially model polyolefin blends cast onto solid substrates, revealed the following picture: Starting from a homogeneous A/B mixture, annealing the sample into the two phase region leads to amplification of concentration fluctuations. The two newly formed coexisting phases of compositions ϕ_1, ϕ_2 separate into two coexisting layers, with the interface between them parallel to the confining walls, that is, the polymer/air and polymer/substrate interfaces (the case of asymmetric confining surfaces, which is the usual case studied to date, generally results in the foregoing picture. However, even asymmetric confinement can sometimes result in a symmetric phase segregation see, e.g., ref.[6,] and papers cited therein). This structure was observed to be thermodynamically stable,[2,4,7,8] despite the fact that the interfacial area between the two phases could be reduced if the interface would be orthogonal to the confining walls, and so should be favored as it would result in a lower interfacial free energy. Theoretical models[9–11] suggest that the origin of the observed layering is the nonsymmetric interaction between the mixture components and the interface: the air interface favors one of the blend components while the substrate attracts the other. The overall free energy then includes the additional interfacial energy terms

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Correspondence to: J. Klein (E-mail: jacob.klein@weizmann.ac.il)

* *Present address:* Institute of Polymers, Department of Materials, ETH Zürich, CNB E 97, Universitätsstraße 6, 8092 Zürich, Switzerland

** *Present address:* Materials Research Science and Engineering Center on Polymers, University of Massachusetts, Amherst, Massachusetts 01003

Journal of Polymer Science: Part B: Polymer Physics, Vol. 38, 831–837 (2000)

relating to the polymer/air and polymer/substrate interfaces. The predicted equilibrium structure[9,10,12] is that of two coexisting phases layering parallel to the confining walls as indeed observed. This argument, on the other hand, does not hold for symmetric boundary conditions where a film is confined between two identical walls. There have, so far, been few experimental studies on the influence of symmetric boundary conditions (b.c.) on the equilibrium configuration of two coexisting phases,[13,14] and none where the composition profiles with respect to the b.c. have been directly measured, mainly because it is not straightforward to arrange such a configuration experimentally. For the case of simple liquids the structure of spinodally decomposed thin films has also been studied by computer simulation methods.[15,16] Here we focus on the experimental investigation of the equilibrium structure and geometry of thin films of binary polymer mixtures confined between identical boundaries. In particular, we investigate the effect of the boundary conditions on the orientation of the interface between the two coexisting phases within the films.

EXPERIMENTAL

Materials

The materials used for the study presented here were random copolymers (polyolefins) of (—C_4H_8—) and [—$C_2H_3(C_2H_5)$—] monomers, as described in detail earlier.[4,17] They were kindly donated by Dr. L. J. Fetters (Exxon). The mean microstructure was $\{(C_4H_8)_{1\text{-}x} - [C_2H_3(C_2H_5)]_x\}_N$ (henceforth designated hx when protonated and dx when deuterated, where x is in %). We used a mixture of d75 and h86 with degrees of polymerization of $N_{86} = 1520$ and $N_{75} = 1625$. The bulk behavior of this couple under nonsymmetric boundary conditions has been well characterized in earlier studies.[4] The critical temperature, the critical volume fraction (of the deuterated component) and the interaction parameter (as deduced from fits to the binodal) are, respectively, $T_c = 97$ °C, $\phi_c = 0.58$, and $\chi(T, \phi) = (0.428/T - 4.9 \times 10^{-5})(1 + 0.277\,\phi)$.[18] The phase coexistence curve for this mixture and the coordinates of our experiment are shown in Figure 1. Polished silicon wafers (P-type, ⟨100⟩ oriented, 6–13 Ω/cm obtained from the Institute of Electronic Materials Technology, Warsaw) were used as supporting substrate for the polymer films. The toluene used was either Frutarum or Merck, analytical grade.

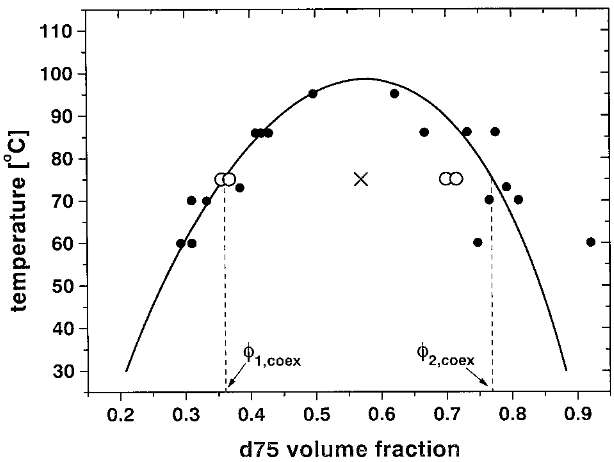

Figure 1. Experimentally determined phase coexistence diagram (binodal) of the blend d75/h86, as determined by NRA.[4] From the binodal, the bulk critical temperature is $T_C = 97 \pm 4$ °C. The solid line represents the best fits to the experimental data, calculated from the Flory–Huggins model with a ϕ dependent interaction parameter $\chi(T, \phi) = (0.428/T - 4.9 \times 10^{-5})(1 + 0.277\,\phi)$. The cross indicates the volume fraction and temperature of our experiments. The open circles are the values of ϕ_μ and ϕ_2 from the profiles of Figure 3.

Sample Preparation

Nonsymmetric Boundary Conditions

A mixture of d75 and h86 was prepared in toluene and spin-cast from solution onto gold-covered silicon wafers to create films of a uniform thickness in the range 300 –400 nm with a volume fraction of $\phi_{d75} = 0.55 \pm 0.01$.

Symmetric Boundary Conditions

In Figure 2 we present schematically the sample configuration used in this part of the study. Thin layers of h86 of a thickness of 100–200 nm were spin-cast from a toluene solution onto gold-covered silicon wafers. Subsequently, the samples were irradiated with a 1.2 MeV ^{3}He beam under an incident angle of 14°. As was shown previously,[19,20] ion fluences of about 10^{14} ions/cm^2 lead to crosslinking of the polymer sufficient to inhibit any detectable in- or out-diffusion of polymer chains.[21] The ion doses we aimed for in our experiments were the minimal that would lead to such inhibition, so as to minimize the extent of chemical changes taking place on irradiation

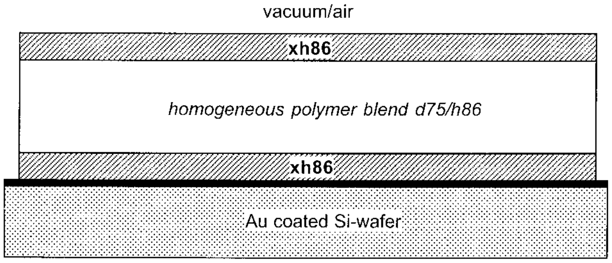

Figure 2. Schematic drawing of the sample configuration used to study the influence of symmetric boundary conditions on the equilibrium structure of thin phase-separated films. On top of a supporting silicon wafer a triple-layer structure was mounted, where the d75/h86 blend is confined between two layers of crosslinked h86 (xh86).

[though occasionally the dose was slightly lower and some slight interdiffusion between wall and free melt took place, see Fig. 4(a) later]. The crosslinked films can thus be regarded as confining walls composed of a material identical to one of the mixture components (h86). The surface of these crosslinked h86 films, henceforth termed xh86, is slightly rougher than as-cast polymer films[22] while JKR-type contact mechanics measurements revealed that the surface energy of the crosslinked layer was unperturbed, indicating that the surface chemistry was essentially unchanged by the irradiation.[20] Films of 300–400-nm thickness of the d75/h86 mixture were spin-cast on freshly cleaved mica and floated directly onto the crosslinked xh86 substrates, as described in detail elsewhere.[4,23] A second 100–200-nm thick layer of xh86, prepared by spin casting and irradiating on freshly cleaved mica was floated off and transferred on top of the xh86-(d75/h86) bilayer, resulting in the final sandwich structure as shown in Figure 2. Such a film thickness of the confining crosslinked layers largely suppresses the long-range interactions due to the silicon substrate.[24,25]

Annealing

After allowing the residual toluene to evaporate, the samples were sealed in ampoules under vacuum ($p < 5 \times 10^{-3}$ Pa) and annealed at 75 °C for up to 27 days. Subsequently, the samples were quenched rapidly to a temperature (< -80 °C) below their glass-transition temperature until measured.

Experimental Technique

Nuclear Reaction Analysis (NRA)[26,27] was used to probe the depth-distribution profiles of the deuterated polymer chains. In this method a monoenergetic ^{3}He beam is incident at a low angle α on the polymer sample, and undergoes the following reaction:

$$^3\mathrm{He} + {}^2\mathrm{H} \rightarrow {}^4\mathrm{He} + {}^1\mathrm{H} + \mathrm{Q}, \quad \mathrm{Q} = 18.35\ \mathrm{MeV} \tag{1}$$

The energy spectrum of the emitted particles, together with the known energy losses, and reaction cross section readily provide the concentration profile $\phi(z)$ of the deuterated chains as function of depth. The spatial resolution of the method depends on the incident energy of the ^{3}He beam, the angle between beam and sample, on the depth within the sample, and on the particles being detected. The best resolution is obtained at the sample surface. In the conditions and configuration used in this study the resolution is typically 14 nm at the sample surface and 80 nm at a depth of 400 nm. We note that the deuterium depth distribution revealed by the NRA technique is laterally averaged over the beam footprint on the sample, which is typically 1 mm by 10 mm in these experiments.

RESULTS AND DISCUSSION

Figure 3(a,b) shows the composition depth profiles of d75/h86 samples after annealing at a temperature of $T = 75$ °C under nonsymmetric boundary conditions for 20 and 27 days, respectively. In both samples it can be seen that the two coexisting phases with $\phi_1 \cong 0.38$, $\phi_2 \cong 0.70$, are aligned parallel to the substrate, with the h86 rich layer adjacent to the air surface and the d75 rich phase along the solid substrate. Within the scatter these observations are in agreement with the earlier experiments of Scheffold et al.,[4] as seen also in Figure 1. Scheffold and coworkers[28] explained the attraction of the h86-rich phase to the air surface by the lower surface tension of the h86 component, resulting from the lower cohesive energies of the pure higher-branched polyolefin.[29] A comparison of the two profiles indicates that annealing times of 20 days or less are sufficient to achieve steady state within the sample thickness range studied here.

The corresponding measurements under symmetric boundary conditions are shown in Figure 4. The composition depth profiles of the d75/h86 samples after annealing at a temperature of T

= 75 °C under symmetric boundary conditions for 20 and 27 days, respectively, differ clearly from those shown in Figure 3. In particular there is no indication of a layered two-phase profile. We find that a distribution uniform within the bulk of the film (dotted line), convoluted with the experimental resolution to yield the solid lines shown, describes the experimental data reasonably well.[30] This fit suggests that, when laterally averaged over the projected cross-sectional area of the ion beam, the concentration of d75 is constant, in marked contrast to the case of asymmetric walls in Figure 3. In the following, we will discuss the possible origin of this observation.

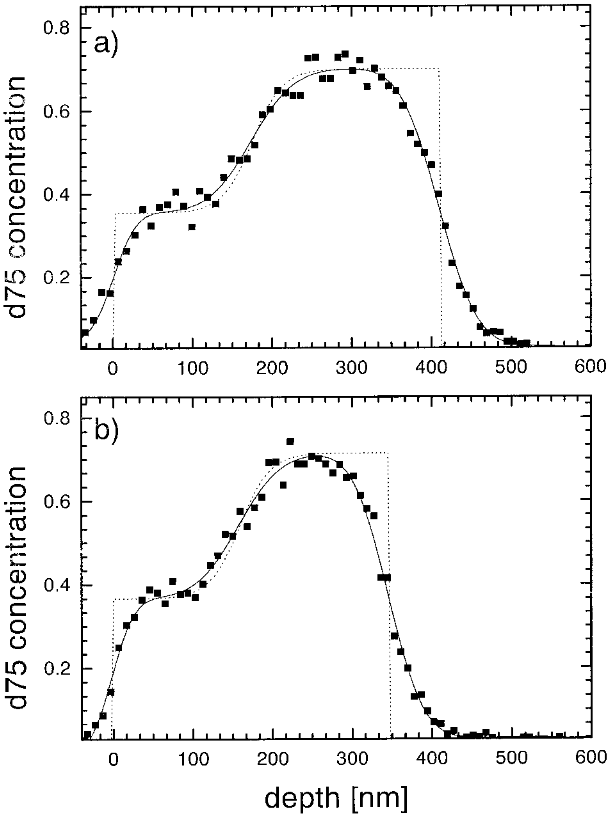

Figure 3. Typical concentration-depth profiles of the d75/h86 blend (55% volume fraction d75) spin cast on gold-covered silicon wafers and exposing its outer surface to vacuum during annealing (nonsymmetric boundary conditions), as measured by NRA. The samples were annealed for 20 and 27 days, respectively, at $T = 75$ °C. In both samples the two coexisting phases with $\phi_1 = 0.38$, $\phi_2 = 0.70$ are aligned parallel to the substrate, with the h86-rich layer adjacent to the surface and the d75-rich phase along the substrate. The dotted curves are the theoretical profiles $\phi(z) = [\phi_1 + \phi_2 + (\phi_2 - \phi_1)\tanh(z - z_0)/w]$, where ϕ_1 and ϕ_2 are the concentrations of the two coexisting phases, z_0 is the midpoint of the interfaces, and w the width of the interface. The solid lines are the best fit to the data obtained by convoluting the theoretical profiles with the independently determined depth dependent resolution.[27]

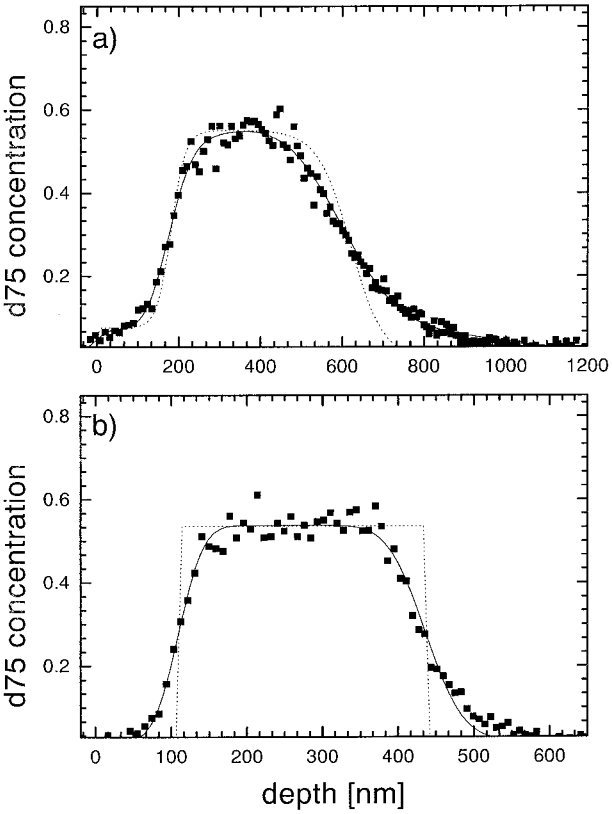

Figure 4. Concentration-depth profiles of the d75/h86 blend (55% volume fraction d75) confined between two xh86 films (symmetric boundary conditions), as measured by nuclear reaction analysis. The samples were annealed for (a) 20 and (b) 27 days, respectively, at $T = 75$ °C. The solid lines are the best fit to the data obtained by convoluting model profiles (the functions indicated by the dotted lines) with the independently determined depth-dependent resolution.[27] In Figure 4. (a) (top), the broadened edges are due to some interdiffusion with the xh86 walls resulting from slightly insufficient crosslinking[30] in this sample.

As the annealing conditions are well within the two-phase regime (× in Fig. 1), we expect demixing into two coexisting phases within the films. A comparison with identical samples annealed under nonsymmetric boundary conditions (Fig. 3) shows that the thermal equilibrium in the normal direction should have been reached by all samples (as also expected from earlier work on diffusion coefficients in these mixtures[31]). A discussion of the possible equilibrium patterns within thin films of confined polymer mixtures, similar to our configuration, was recently developed by Binder and coworkers.[10,11,32] By applying mean-field calculations[32] and Monte Carlo simulation techniques,[11] Binder et al. investigated the theoretical equilibrium configurations of *A*/*B* polymer blends as a function of the boundary conditions and of the location of the blend temperature in relation to the bulk critical temperature T_c and the wetting transition temperature T_w. Flebbe, Dünweg and Binder[32] extended the earlier mean-field calculations of Schmidt and Binder,[33] which treated only the extended (semi-infinite) case, to the geometry of a thin film of thickness D. They assumed that the free energy of an incompressible polymer mixture in the case of symmetric boundary conditions in the long wavelength approximation can be written as:

$$\frac{\Delta F}{k_B T} = \int_0^D dz \left[f[\phi(z)] + \frac{a^2}{36\phi(z)[1-\phi(z)]} \left[\frac{d\phi(z)}{dz} \right]^2 \right] + f_s^{(\text{bare})}(\phi_0) + f_s^{(\text{bare})}(\phi_D) \quad (2)$$

where a is the statistical segment length, f is the free-energy density in the bulk, $f_s^{(\text{bare})}$ are the bare surface contributions to the surface excess free energy, and ϕ_0 and ϕ_D are the concentrations at the two polymer/wall interfaces. The free energy density f was assumed to be the standard Flory–Huggins expression, where

$$f(\phi) = (\phi/N_A)\ln \phi + ((1-\phi)/N_B)\ln \phi + \chi\phi(1-\phi) \quad (3)$$

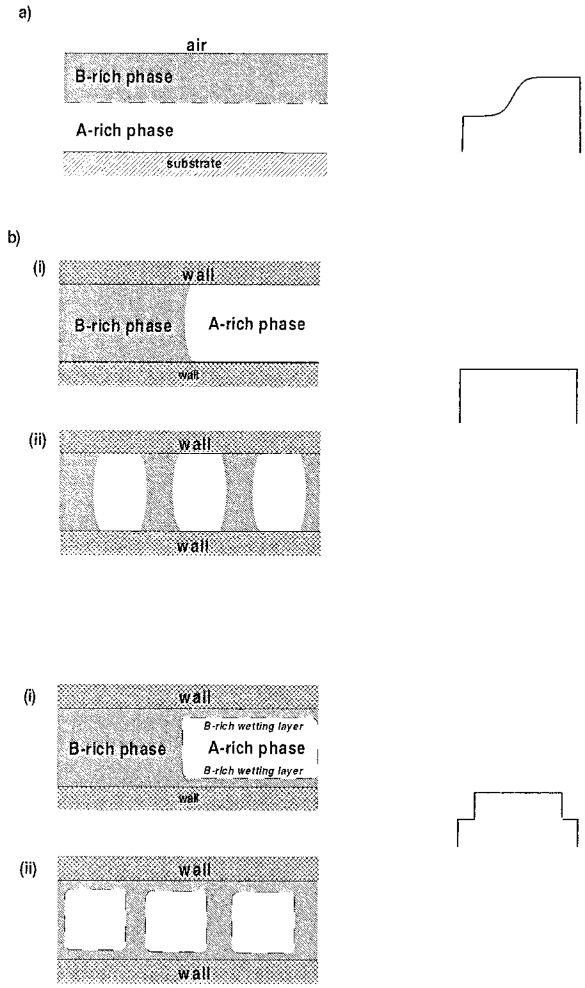

Figure 5. (Left side) Schematic drawings of the equilibrium configurations of thin phase-separated films, as predicted by the model of Binder et al.[10,11,32] Figures (a-c) show the predicted configurations and concentration depth profiles in the case of (a) nonsymmetric boundary conditions, equilibrium situation; (b) symmetric boundary conditions and $T < T_w$, (i) equilibrium situation, (ii) nonequilibrium configuration; (c) symmetric boundary conditions and $T > T_w$, (i) equilibrium situation, (ii) nonequilibrium configuration. The RHS shows schematically the composition-depth profiles expected if the configurations shown on the LHS are averaged over the entire film.

We consider qualitatively the predictions of this model relevant to our configuration. Figure 5(a) shows the equilibrium configuration expected in a phase-separated blend below T_c confined between nonsymmetric walls, where one of the phases is preferred at one of the walls. The predicted composition depth profile from this layered configuration is similar to the experimental ones shown in Figure 3 (and observed in many earlier studies[3,5]) for nonsymmetric confinement of similar polyolefin mixtures. In the case of symmetric boundary conditions and $T < T_c$ two possible configurations are predicted, depending on the coordinates of the system in the phase coexistence curve in relation to T_w. At temperatures below T_w the interface between the two phases is perpendicular to the walls and—if the walls have a preference for one of the phases—meets the walls at a nonzero contact angle [Fig. 5(b)(i)], reflecting partial wetting. One also expects at each wall a thin enrichment layer of the surface preferred phase. Above T_w the contact angle is zero (complete wetting), which leads to a wetting layer of the phase favored by the wall [Fig. 5(c)(i)]. These predicted equilibrium structures can be understood qualitatively as follows: The cost of interfacial free energy between the coexisting phases is proportional to the interfacial tension γ multiplied by the total area of the interface. Because the lateral dimensions of thin films are much larger than the dimensions perpendicular to the confining walls, the area of the interface between the coexisting phases is smaller when the interface is vertical, so that the interfacial energy will be minimized by an interface as sketched in Figure 5(b)(i).

Earlier studies of similar polyolefin blends[3,5] indicated that the wetting temperature T_w in such systems at the polymer/air interface could be far (100 °C or more) below the critical temperature T_c. In our system, however, contact is with the xh86 surface. Recent experiments[23] for comparable polyolefin blends (in the miscible regime of the phase diagram), in contact with a wall composed of a crosslinked layer of one of the mixture components, suggest that there is only a weak preference, if any, of this wall to either pure component. Therefore, we might expect only partial wetting of the xh86 surface by one of the phases, and equilibrium composition depth profiles similar to the one shown in Figure 5(b)(i), rather than that of Figure 5(c)(i). If complete wetting by the h86-rich phase was to take place at the xh86 surface, however, so that the picture of Fig. 5(c)(i) [or Fig. 5(c)(ii), see later] was to apply, it is possible that this would be revealed by our profiles. In a finite film where the amount of material of each phase is conserved, and where the lateral dimensions of the phase-separated regions are much larger than the film thickness, it is easy to show[13] that the wetting layers near the confining walls would tend to thin in order to minimize the interfacial contact between the coexisting phases. The limiting thickness of these layers would be of order of the correlation length or intrinsic interfacial width between coexisting phases. It is possible that we would be able to resolve such a layer by NRA, even through the crosslinked wall cover, at least for the case of the outer wall/mixture interface. The absence of such an observed (thin) wetting layer speaks in favor of the structure shown in Figure 5(b).

A point open for discussion is whether the equilibrium picture of Binder et al., where the film is divided into two lateral regions, provides a correct description of our observation. It is very likely that, as in dewetting processes, which lead to an array of small droplets on a substrate even when one big droplet might be energetically favorable, phase separation under symmetric boundary conditions might lead to an array of inclusions, or patches of one phase within the other.[13,15,34] The corresponding configurations are those shown schematically in Figure 5(b)(ii) and 5(c)(ii) for the nonwetting and wetting case, respectively. The relaxation to the thermal equilibrium configuration, which consists of only two large domains (the limit considered in the model), driven by the need to minimize the surface tension in an Ostwald-ripening fashion, would then require chain diffusion over distances comparable with the lateral dimensions of the film. As such, it would be too slow a process to be observed in our experiments. For a distribution of droplets sampled and averaged across the NRA beam cross section, the profiles corresponding to Figure 5(b)(ii) or 5(c)(ii) would indeed resemble the measured profiles shown in Figure 4 (though a more direct measure of lateral structure, to be carried out in future studies, would clearly provide important complementary information). We note that other theories[35,36] propose nonsymmetric composition depth profiles even for symmetric boundary conditions and so do not appear to explain our results.

CONCLUSIONS

We investigated the role of symmetric confining walls on the phase separation process of thin films of polymer blends. We observed that even after annealing times, which were sufficient to bring comparable samples into thermal equilibrium and a layered configuration under nonsymmetric boundary conditions, the laterally averaged concentration in the symmetric case is still constant. Our results indicating a uniform composition in the film are probably due to averaging over an area with many droplets of one phase in the other, and suggest that the equilibrium structure of phase-separated thin films confined between identical walls is characterized by an interface between the two phases running perpendicular to the two walls.

The authors are grateful to Dr. Lewis J. Fetters for donating the polymer samples described in this study. They thank K. Binder and B. Dünweg for useful discussions, and the German-Israel Foundation (GIF), the Israel Science Foundation and the Israeli Ministry of Science (Tashtiot grant) for financial support.

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where $A_{\mathrm{x/y}}$ are the different Hamaker constants. Thus, for the liquid polyolefin mixture on top of a $d = 200$-nm thick crosslinked polyolefine film, the interactions (at say the midplane of the film at h = 200 nm) are largely due to the crosslinked film and not to the underlying silicon substrate.
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