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Surface-Directed Spinodal Decomposition in the Blend of Polystyrene and Tetramethyl-Bisphenol-A Polycarbonate[†]

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1. Introduction

When a bulk polymer blend is quenched inside the spinodal of the two-phase region, the concentration fluctuations grow as spinodal decomposition occurs. The resulting composition waves have wave vectors in all directions in space, resulting in an isotropic structure. However, in the presence of a surface with a preferential attractive interaction for one of the components, segregation of that component to the surface also starts to occur. A concentration gradient is created normal to the surface, and, in turn, propagation of a coherent concentration wave with a dominant wave vector normal to the surface is induced.[1] The layered structure thus formed should have dramatically different near-surface properties. This phenomenon—which is called surface-directed spinodal decomposition—has recently attracted a significant amount of interest both experimentally[1-4] and theoretically.[5-8]. However, previous experiments have been limited to model polymer blends which show upper critical solution temperature (UCST) behavior, whereas most practical miscible polymer blends show lower critical solution temperature (LCST) behavior. In this report, we examine the concentration profiles in thin films of blends of deuterated polystyrene (d-PS) and tetramethyl-Bisphenol-A polycarbonate (TMPC) when these films are up-quenched into the two-phase region above the LCST[9,10] (~240 °C). The focus will be on the effect of film thickness.

2. Experimental Section

The mixtures of d-PS (molecular weight M_w = 489 000 with a polydispersity index PD < 1.1) and TMPC (M_w = 42 000 with PD = 2.9 or M_w = 76 000 with PD = 5.9) were dissolved in anisole (methoxybenzene). The volume fraction of d-PS was chosen to be 0.4 or 0.45, which has been observed to be close to the critical composition.[10] Films were prepared by spin casting from the solution onto the native oxide surface of silicon wafers. Some films were deposited on a surface of a self-assembled monolayer formed from octadecyltrichlorosilane (OTS) on the native oxide of silicon. In this case, forming the film by spin casting was impossible because all the solution slipped off of the surface during the spinning process. In these circumstances, the film was prepared by spin casting a solution onto a glass slide and then floating it off onto the surface of a deionized water bath, from where it was then picked up onto the OTS–Si substrate. These films were up-quenched into the two-phase region (263 or 250 °C) under an Ar atmosphere, held for a time to allow spinodal decomposition to occur, and then cooled to room temperature. The composition profiles were obtained using conventional and time-of-flight (TOF) forward recoil spectrometry (FRES) with $^4\mathrm{He}^{2+}$ ions as incoming particles.[11] Using unannealed films of various thicknesses, the depth resolution for TOF-FRES was determined to be represented by a Gaussian function whose full width half-maximum (fwhm) increased with depth z from the air surface. A fwhm of $30 + 0.135z$ nm was obtained: The resolution right at the surface was nearly 3 times smaller than that of conventional FRES (fwhm = 88 nm). Both deuterium and hydrogen profiles were obtained.

3. Results and Discussion

Figure 1 shows the volume fraction versus depth profiles for both d-PS and TMPC in the films of 45 vol % d-PS blended with 42 000 molecular weight TMPC (a) deposited on a native silicon oxide substrate and annealed at 263 °C for 10 min and (b) deposited on OTS-coated Si substrate and annealed at 263 °C for 5 min. Distinct composition waves normal to the surface are seen as compared with the concentration profiles before annealing (broken and dotted lines). It was found that d-PS was attracted to both the air and the OTS–Si surfaces and that TMPC was attracted to the native silicon oxide surface.

We then studied the thickness dependence in blends of d-PS (40 vol %) and 76 000 molecular weight TMPC which were prepared on a native silicon oxide substrate and annealed at 250 °C for 30 min. The volume fraction of d-PS versus depth profiles due to surface-directed spinodal decomposition for films of various thicknesses are shown in Figure 2. We tried to represent the data by summing two separate damped cosine functions, one originating from each surface. Such functions were shown by Krausch et al.[3] to fit similar composition profiles in the isotopic blend of deuterated poly(ethylenepropylene) and poly(ethylenepropylene) (d-PEP and PEP). The damped cosine wave from the air surface, $\phi_{\mathrm{surf}}(z)$, and that from the native silicon oxide surface, $\phi_{\mathrm{int}}(z)$, as a function of depth z from the surface are given by

$$\phi_{\mathrm{surf}}(z) = 0.4 + \phi_{\mathrm{surf;0}} \exp\left(-\frac{z}{\zeta_{\mathrm{surf}}}\right) \cos\left(\frac{2\pi z}{\lambda_{\mathrm{m}}}\right) \tag{1.1}$$

$$\phi_{\mathrm{int}}(z) = 0.4 - \phi_{\mathrm{int;0}} \exp\left(-\frac{d-z}{\zeta_{\mathrm{int}}}\right) \cos\left(\frac{2\pi(d-z)}{\lambda_{\mathrm{m}}}\right) \tag{1.2}$$

where d, λ_{m}, $\phi_{\mathrm{surf;0}}$ (and $\phi_{\mathrm{int;0}}$), and ζ_{surf} (and ζ_{int}) represent the thickness of the film, the characteristic wavelength of oscillation, the amplitude of the volume fraction at the air surface (and at the native silicon oxide surface), and the characteristic decay length at the air surface (and at the native silicon oxide surface), respectively. The overall concentration profile $\phi_{\mathrm{d\text{-}PS}}(z)$ for d-PS, shown as a solid line in Figure 3 (for 600 nm thick film using the same parameters as in the simulated profiles shown in Figure 2; see below), is obtained by summing $\phi_{\mathrm{surf}}(z)$ (shown in the left oscillating part of the solid line in Figure 3) and $\phi_{\mathrm{int}}(z)$ (shown in the right oscillating part of the solid line in Figure 3) and subtracting off the initial volume fraction of 0.4 so it is not counted twice.

$$\phi_{\mathrm{d\text{-}PS}}(z) = \phi_{\mathrm{surf}}(z) + \phi_{\mathrm{int}}(z) - 0.4 \tag{2}$$

The $\phi_{\mathrm{d\text{-}PS}}(z)$ given by eq 2 was then convolved with a Gaussian with a depth-dependent fwhm (=$30 + 0.135z$ nm) to account for the instrumental resolution of TOF-FRES. The concentration profile $\phi_{\mathrm{TMPC}}(z)$ for TMPC (=1

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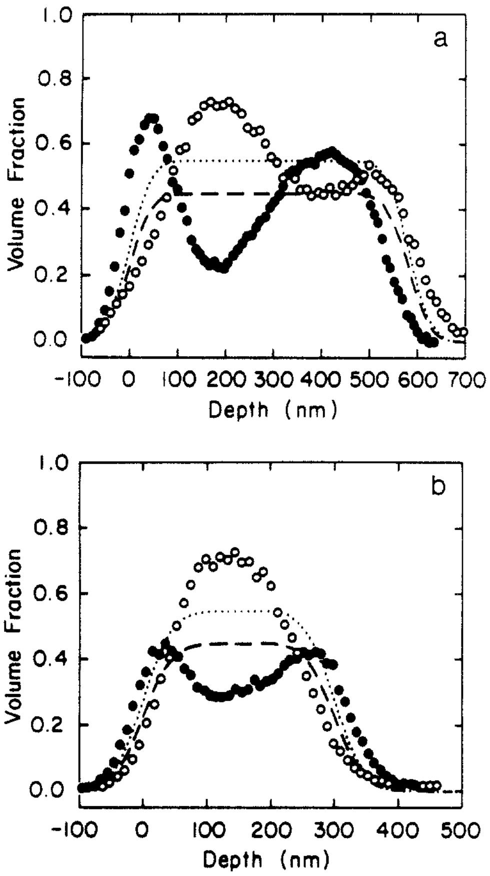

Figure 1. Volume fraction versus depth profiles for both d-PS (filled circles) and TMPC (open circles), $\phi_{d\text{-PS}}(z)$ and $\phi_{TMPC}(z)$, in the blend of 45 vol % of 489 000 molecular weight d-PS and 55 vol % 42 000 molecular weight TMPC as determined by conventional FRES. (a) A 580 nm thick film on a native silicon oxide substrate was annealed at 263 °C for 10 min under an Ar atmosphere. (b) A 300 nm thick film on the OTS-coated Si substrate was annealed at 263 °C for 5 min under an Ar atmosphere. The broken and dotted lines represent the volume fraction profiles before annealing for d-PS and TMPC, respectively ($\phi_{d\text{-PS}}(z) = 0.45$ and $\phi_{TMPC}(z) = 0.55$), which could be fit by convolving a uniform composition film of this thickness with a Gaussian with an independently measured full width half-maximum (fwhm) of 88 nm.

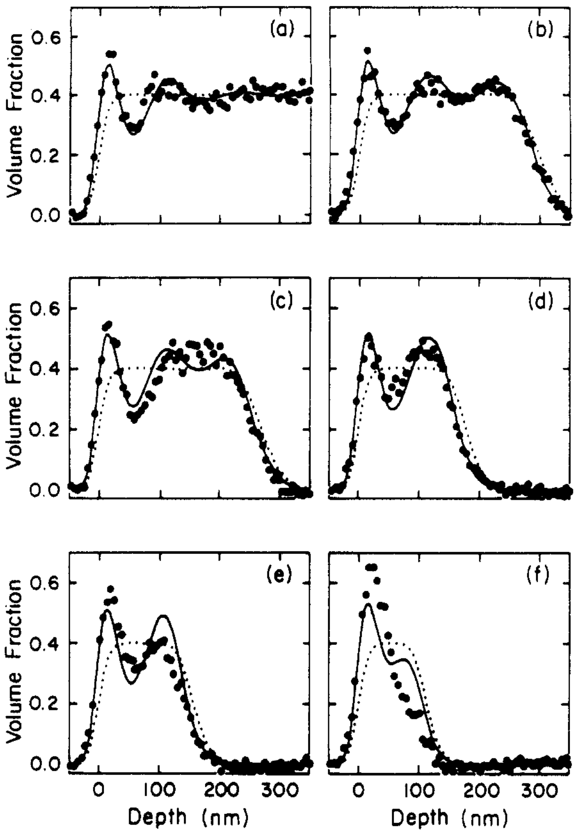

Figure 2. Volume fraction versus depth profiles of d-PS, $\phi_{d\text{-PS}}(z)$, for different film thicknesses d in the blend of 40 vol % 489 000 molecular weight d-PS and 60 vol % 76 000 molecular weight TMPC as determined by TOF-FRES. All samples were prepared on the native silicon oxide substrates and were annealed at 250 °C for 30 min under an Ar atmosphere. (a) $d > 1000$ nm, (b) $d = 298$ nm, (c) $d = 270$ nm, (d) $d = 178$ nm, (e) $d = 157$ nm, and (f) $d = 113$ nm. The dotted lines represent the volume fraction profiles before annealing ($\phi_{d\text{-PS}}(z) = 0.4$) which were convolved with a Gaussian with a depth-dependent full width half-maximum (fwhm) of $30 + 0.135z$ nm. The parameters used for determining the oscillating profile (solid lines) are explained in section 3.

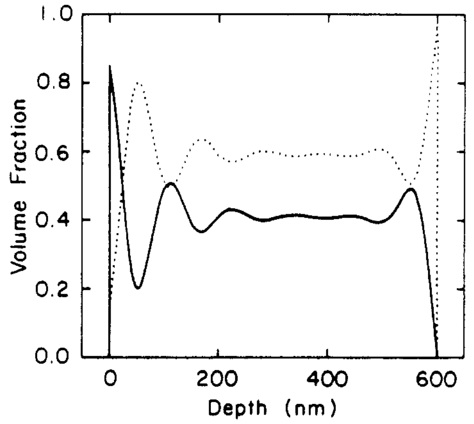

Figure 3. Volume fraction versus depth profile for d-PS, $\phi_{d\text{-PS}}(z)$, obtained according to eq 2 (solid line) in the blend of 40 vol % d-PS and 60 vol % TMPC when film thickness d is 600 nm. The dotted line represents the TMPC volume fraction, $\phi_{TMPC}(z)$, which is $1 - \phi_{d\text{-PS}}(z)$. The parameters used for determining the profile are explained in section 3.

$- \phi_{d\text{-PS}}(z)$) is also drawn as a dotted line in Figure 3. Using sufficiently thick films in which two waves do not interfere as shown in Figure 2a,b, λ_m could be determined to be about 115 nm. However, due to the limited instrumental resolution, it was impossible to precisely determine $\phi_{surf;0}$ and $\phi_{int;0}$ directly from the depth profiles; thus these were determined from the following argument. The fastest growing wavelength in the bulk in the initial stages of spinodal decomposition could be calculated from the temperature dependence and composition dependence of the Flory interaction parameter, χ, which were obtained in recent diffusion studies.[10] It is estimated that the spinodal temperature is about 240 °C and the value of χ at the spinodal, χ_s, is 2.6×10^{-3}, while χ at 250 °C is 7.9×10^{-3}. These values, together with the component chain dimensions, gave a bulk characteristic wavelength $L_m = 2\pi/q_m$ of 48 nm, where q_m is the wave vector of the dominant mode of the fluctuation given as[12]

$$q_m = \left(\frac{3(\chi - \chi_s)}{\dfrac{R_{g,d\text{-PS}}^{\;2}}{N_{d\text{-PS}}\phi_{d\text{-PS}}} + \dfrac{R_{g,TMPC}^{\;2}}{N_{TMPC}\phi_{TMPC}}} \right)^{1/2} \tag{3}$$

The radii of gyration for d-PS and TMPC, $R_{g,d\text{-PS}}$ and $R_{g,TMPC}$, used were 18.5 and 10.5 nm, respectively.[13] We note that λ_m is significantly larger than the above value of L_m, from which we judge that the process is well past the initial stages of spinodal decomposition. Thus the compositions of two phase-separated domains could be approximated as the binodal compositions. The independently measured binodal volume fractions of d-PS[10] (about 0.83 and 0.03 at 250 °C) were thus used for the compositions at the air and the native silicon oxide surface, from which the values of $\phi_{\mathrm{surf;0}}$ and $\phi_{\mathrm{int;0}}$ were determined to be 0.43 and 0.37, respectively. From Figure 2a–d, the decay lengths ξ_{surf} and ξ_{int} could then be roughly estimated to be 75 and 35 nm, respectively. The ξ_{int} value is quite uncertain since the structure of the concentration profile at the native silicon oxide surface was difficult to resolve because the instrumental resolution deep in the film becomes rather poor. Using the same parameters except the thickness, the solid lines in Figure 2 were drawn. Reasonable agreement with eq 2 is observed.

Our depth profiling technique allows us to monitor a composition versus depth that is averaged laterally over the size of the $^4\mathrm{He}^{2+}$ ion beam ($\sim$10 mm^2). Isotropic demixing processes also compete with the growth of the surface-directed spinodal decomposition profile. Below a certain depth, such processes eventually become dominant,[3] and the laterally averaged concentration gradient normal to the surface will tend to zero. If, however, we decrease the thickness of the film below a characteristic length, the coarsening process is expected to be dominated by the effect of the boundary surfaces, and therefore deviations from eq 2 may be expected. In similar experiments of Krausch et al. using d-PEP and PEP,[3] the superposition of eq 2 was observed to fail when the film thickness became less than $1.5\lambda_{\mathrm{m}}$. In Figure 2d–f are the cases when d is $1.55\lambda_{\mathrm{m}}$, $1.37\lambda_{\mathrm{m}}$, and $0.98\lambda_{\mathrm{m}}$, respectively. We observe that for thicknesses less than $1.5\lambda_{\mathrm{m}}$ the film tends to decompose into a bilayer in which there is a d-PS-rich domain at the air surface overlying a TMPC-rich one formed at the native oxide surface. The formation of this bilayer is nearly complete in the thinnest film (Figure 2f). In the case of Figure 2f, the whole film can be thought of as being under surface fields from both sides with different signs so that the lateral demixing process is not observed. Closer investigation into this effect would be of interest in revealing the kinetic nature of the phase separation when the film thickness is less than or comparable to $1.5\lambda_{\mathrm{m}}$.

4. Conclusions

(1) We have observed surface-directed spinodal decomposition in a miscible polymer blend (d-PS/TMPC) with a lower critical solution temperature. The process of surface-directed spinodal decomposition thus is a general phenomenon found regardless of whether the system has an UCST or LCST.

(2) In thin films of blends of d-PS and TMPC on silicon wafers, d-PS tends to segregate to the air surface and TMPC to the native silicon oxide surface. Modifying the Si surfaces with OTS to form a paraffin-like self-assembled monolayer causes d-PS to segregate to both surfaces of the film.

(3) For d-PS/TMPC blends on native silicon oxide surfaces the surface-directed spinodal decomposition waves from the two surfaces begin to interfere as the film thickness is decreased. Below a film thickness of about 1.5 times the wavelength obtained in thick films, there is a strong tendency to form a bilayer consisting of a d-PS-rich domain on the air surface and a TMPC-rich domain on the native silicon oxide surface.

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