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Phase Separation of a Polymer Mixture Driven by a Gradient of Light Intensity

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The stability of a physicochemical system under thermodynamic equilibrium is dictated by the Gibbs free-energy minimum.[1] So far, most of the experiments as well as theories on phase separation of polymer mixtures have been performed under thermodynamic equilibrium where the variables such as pressure, composition, and temperature (P,V,T) are kept constant.[2,3] In practice, phase separation often occurs under thermodynamic nonequilibrium conditions. For example, materials processing is performed under large scales where thermodynamic variables are no longer constant[4,5] and can either vary with time or exist as a spatial distribution. The system is thus far from equilibrium, and phase separation becomes a spatiotemporal phenomenon.[6] Basic knowledge of these time-evolution processes would be helpful for quality control of the final products.

We have studied phase separation of poly(2-chlorostyrene)/poly(vinyl methyl ether) (P2CS/PVME) blends induced by a temperature gradient.[7] However, the experimental observation was limited by the thermal decomposition of PVME on the high temperature side of the gradient and particularly by the very fast phase separation kinetics taking place in these high-temperature regions. In this communication, we report a preliminary result on the morphology and phase separation kinetics of *trans*-stilbene-labeled polystyrene/poly(vinyl methyl ether) (PSS/PVME) blends resulting from irradiation with a gradient of ultraviolet (UV) light intensity. Previous studies on the miscibility of this particular blend using small-angle neutron scattering (SANS) indicated that trans → cis photoisomerization of stilbene labeled on polystyrene chains can induce phase separation by changing both the segmental volumes of the PSS chains and the enthalpic interactions between the cis-isomer-labeled polystyrene and PVME.[8]

Samples are mixtures of *trans*-stilbene-labeled polystyrene (PSS, $M_w = 2.8 \times 10^5$, $M_w/M_n = 2.2$) and poly(vinyl methyl ether) (PVME, $M_w = 1.0 \times 10^5$, $M_w/M_n = 2.3$). The chemical synthesis of these polymers, the phase behavior, and the preparation procedure of their blends as well as the details of irradiation experiments are described elsewhere.[9] In brief, the average label content is one stilbene per 25 repeat units of a PSS chain, which is equivalent to ca. 4 mol % of PSS. PSS/PVME blends with the thickness 50 μm were sandwiched between two quartz plates and were first equilibrated at 90 °C (15 °C below the cloud point) in the miscible region. Then phase separation was induced by irradiation with 313 nm UV light from a 500 W Hg−Xe lamp (Hamamatsu Photonics). Owing to the trans (1) → cis (2) photoisomerization of stilbene shown below, the miscibility gap of the blend is reduced, and the phase boundary moves toward the low-temperature side.[8]

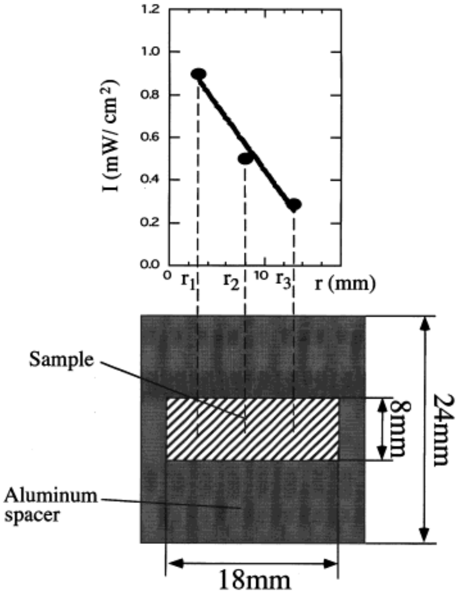
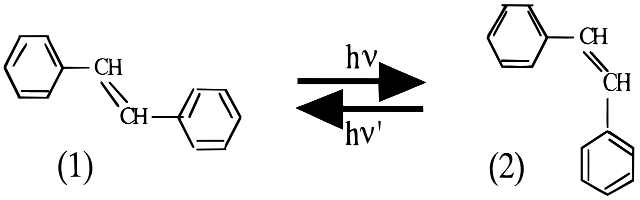


Figure 1. Schematical presentation of the UV light gradient in correspondence with the position of the photoreactive blend. $I_1 = 0.9$, $I_2 = 0.5$, and $I_3 = 0.3$ mW/cm^2; (r_1) = 3, (r_2) = 8, and (r_3) = 13 mm.



Eventually, phase separation takes place as soon as the phase boundary crosses the experimental temperature. The gradient of the UV light imposed on the blend was generated by using a linear wedge neutral density filter (Koyo Inc., Japan) placed between the light source and the sample. The light intensity passing through the filter is approximately a linear function of distance with the gradient of approximately 0.6 mW/cm. As illustrated in Figure 1, the phase separation of PSS/PVME blends under this gradient was monitored at three positions designated as (r_1), (r_2), and (r_3) which are 3, 8, and 13 mm separated from the left edge of the sample taken as the origin. The morphology was observed and analyzed according to the procedure described previously.[9] Briefly, the optical images of the morphology observed under a phase-contrast optical microscope (Nikon, model XF-NTF-21) were digitized and analyzed by two-dimensional fast Fourier transform (2D-FFT) using the softwares Scion Image.[10] The characteristic length scale ξ of the morphology was calculated from the Bragg condition $\xi = 2\pi/q_{\max}$, where $q_{\max}$ is the wavenumber corresponding to the maximum Fourier intensity obtained by sector-averaging the 2D-FFT power spectra. Because phase separation only occurs when the reaction conversion exceeds a threshold, the thermodynamic

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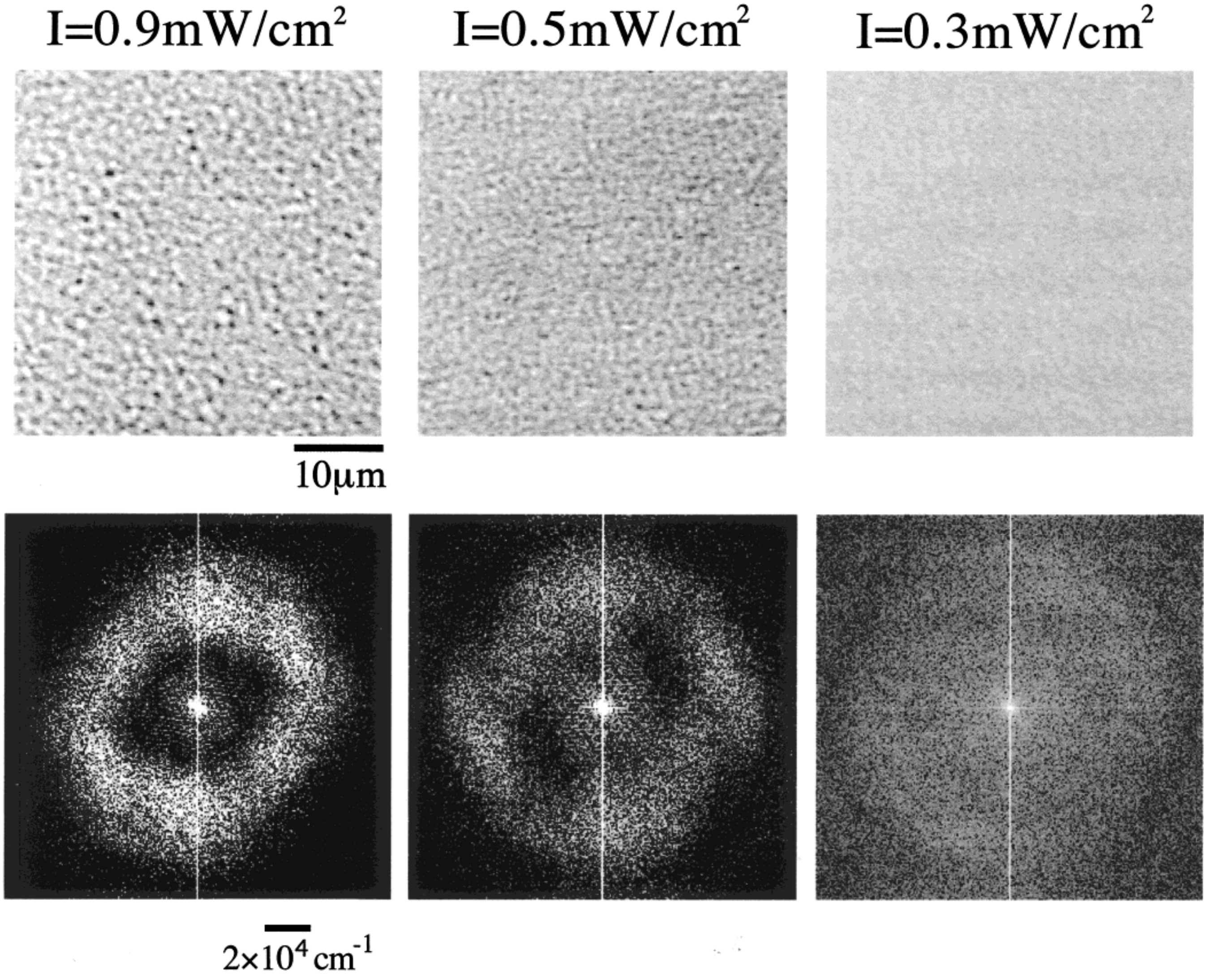

Figure 2. Morphology and the corresponding 2D FFT power spectra observed at three positions (r_1), (r_2), and (r_3) along the gradient of UV light intensity for a PSS/PVME(20/80) blend irradiated in 180 min at 90 °C.

stability of the blend depends critically on the light intensity along the gradient. The kinetics of phase separation was obtained by analyzing the morphology of the blend observed at three positions (r_1), (r_2), and (r_3) which correspond respectively to 0.9, 0.5, and 0.3 mW/cm^2. Figure 2 shows the morphology and their corresponding 2D-FFT power spectra for a PSS/PVME-(20/80) blend irradiated with the light gradient in 180 min. Compared to the case of uniform intensity, the morphology observed in the presence of the gradient is slightly anisotropic. Furthermore, phase separation occurs earlier at the position (r_1) and much later at (r_3). For 180 min of irradiation, the blend at the position (r_3) is still miscible whereas phase separation already proceeds to a considerable extent at the position (r_1). The reaction yield prior to phase separation was estimated by monitoring the photoisomerization kinetics of *trans*-stilbene in three PSS/PVME (20/80) blends irradiated separately with three *uniform* intensities 0.3, 0.5, and 0.9 mW/cm^2. From these results, it was found that the blend becomes cloudy at these three locations after 75, 120, and 140 min of irradiation, respectively. The trend of the reaction kinetics is in accordance with the morphological results shown in Figure 2, revealing that phase separation of PSS/PVME blends only starts as the trans → cis photoisomerization of stilbene exceeds a certain critical conversion upon irradiation. The time evolution of phase separation induced by a gradient of UV light and by *uniform* intensity at 90 °C is summarized in Figure 3 where the characteristic length scale ξ of the morphology observed at three positions (r_1), (r_2), and (r_3) was plotted versus irradiation time together with the results obtained by using a *uniform* intensity. ξ, for both cases, is almost unchanged with irradiation time (t) at the early stage of phase separation. Subsequently, it increases as $\xi \sim t^{\alpha}$ where the exponent α can be considered as an indicator for the rate of the phase-separation process. Eventually, the morphology becomes unchanged with reaction time, and the phase separation is terminated with a stationary modulated structure whose characteristic length scale is determined by the competition between reaction and phase separation. Similar behavior was reported previously for PSS/PVME blends irradiated with *uniform* intensities.[9] Under this particular condition, ξ increases with $\alpha = 0.27-0.28$, which is almost independent from the light intensity within the range 0.3−0.9 mW/cm^2. In the presence of a gradient of light, α varies with the distance from the left edge on the blend. At the upper position of the gradient (0.9 mW/cm^2), it is smallest ($\alpha = 0.35$) and is close to the exponent predicted by the Lifshitz−Slyosov−Wagner (LSW) law.[11,12] On the other

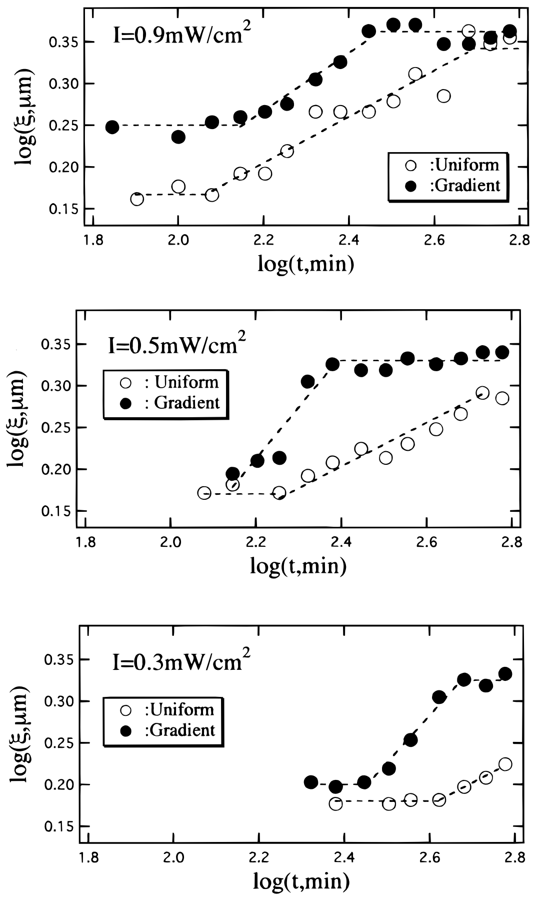

Figure 3. Time evolution of the characteristic length scales observed at 90 °C for a PSS/PVME (20/80) blend irradiated with the intensity gradient (●) and *uniform* intensity (○). The light intensity for both cases is indicated in the figures. $\alpha = 0.27-0.28$ for the uniform intensity; $\alpha = 0.35$ for $I = 0.9$ mW/cm^2; $\alpha = 0.6$ for $I = 0.5$ and 0.3 mW/cm^2 in the presence of the gradient.

hand, α becomes much larger ($\alpha = 0.6$) at the positions (r_2) and (r_3) irradiated with lower intensity. Since during irradiation there exists a *phase separating front* propagating from the upper stream (high intensity) toward the downstream (low intensity) of the gradient, phase separation under an intensity gradient satisfies the conditions of a shallower quench compared to the case of uniform intensity. This leads to the morphology with larger length scales though some uncertainty might accompany the weak contrast at the early stage of phase separation. Furthermore, phase separation in the region close to the leading edge (with the highest intensity) almost satisfies the condition of a *conserved* system, whereas far from this edge (in the regions with lower intensity), the kinetics is affected by the phase separating front and might become *nonconserved*, giving rise to the larger exponent α. Such interference processes of thermodynamic instabilities arising from spatially inhomogeneous phase separation have been observed previously in polymer blends irradiated with linearly polarized light.[13,14] From the viewpoint of practical applications, these experimental results provide not only insight into manufacturing polymeric materials with variable gradients of periodic structure but also useful information for controlling morphology of polymer blends during processing.

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