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Symmetry breaking in phase separation of binary polymer mixtures induced by linearly polarized light

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Symmetry breaking of concentration fluctuations was found in a binary polymer mixture with one component photo-cross-linked by linearly polarized light. As the reaction proceeds, the mixture undergoes phase separation, exhibiting lamellar morphologies with the direction closely perpendicular to the polarization (E) of the exciting light. It was also found that the phase separation is suppressed in the parallel direction and its kinetics strongly depends on the relative orientation with respect to the exciting polarization. Thus, these reacting mixtures provide a model system to study the directional phase separation driven by chemical reactions. [S1063-651X(98)51002-1]

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Phase separation in chemically reacting mixtures [1], particularly in systems driven by reversible chemical reactions, is a fascinating critical phenomenon because the resulting morphology is a consequence of the competition between phase separation and chemical reactions [2–5]. These structures, which are known as modulated phases, share many common features and have been experimentally found in a variety of chemical and physical systems [6]. From the viewpoints of materials science, understanding the formation processes of these modulated phases would give some new insights into morphology control, one of the long-standing research subjects in both polymer science as well as metallurgy. Recently, these particular structures were experimentally observed in polymer mixtures with photo-cross-linking [7,8], photoisomerization [9] reactions, and in thermally polymerizing systems [10,11] as well. In these works, the development of the instabilities triggered by the chemical reactions is spatially symmetric, translationally as well as rotationally invariant.

In this paper, we report the symmetry-breaking phenomena associated with phase separation of binary polymer mixtures photo-cross-linked by linearly polarized light. It is experimentally shown that, due to the selection of the unstable modes by the exciting polarized light, the concentration fluctuations developing in the reacting mixtures become anisotropic, leading to the formation of lamellar structures on the micrometer scale.

Samples used in this work are mixtures of polystyrene derivatives and poly(vinyl methyl ether). To be able to photo-cross-link only one polymer component in the binary mixture, the polystyrene derivative was labeled with the photo-cross-linker anthracene. Preparation as well as characterization of the samples used in this work were already reported in detail elsewhere [12]. The weight-average molecular weights of the anthracene-labeled polystyrene (PSA) and poly(vinyl methyl ether) (PVME) are $M_w = 3.2\times 10^5$ and 9.6×10^4, respectively. The molar fraction of anthracene in PSA is 2.7%, which approximately corresponds to 1 anthracene per 40 repeat monomer units of the polymer.

The cloud points ($T_{\rm cl}$) obtained by light scattering after extrapolating the data to zero-heating rate are illustrated in Fig. 1, showing that the PSA/PVME mixture possesses a lower critical solution temperature (LCST). Photo-cross-linking reactions using photodimerization of anthracene moieties labeled on PSA chains were performed with a high-pressure Hg-Xe lamp (500 W, Hamamatsu Photonics). Linearly polarized light with wavelengths mainly at 365 nm was selected by using a polarizer (HNP'B, Polaroid Inc.) and appropriate optical filters. The details of the optical arrangements for these irradiation experiments were reported previously [8]. The intensity at 365 nm was adjusted at 3 mW/cm^2 by using a convex lens and neutral density filters.

The morphology of the cross-linked blends was observed by using a phase contrast and a differential interference optical microscope (Nikon, XF-NTF-21, Japan) linked to a digital image analyzer (Pias Inc., LA-525, Japan) for further structural analysis. The focus was adjusted at the center of

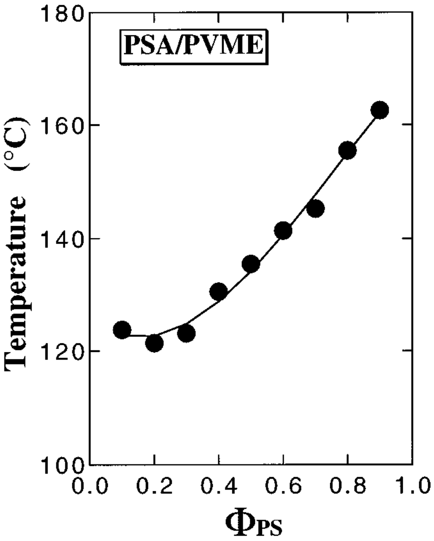

FIG. 1. Composition dependence of the cloud points ($T_{\rm cl}$) of the PSA/PVME mixtures used in this work.

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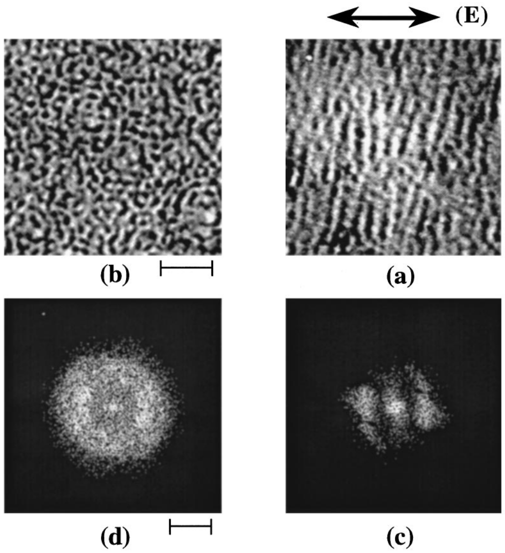

FIG. 2. Phase-contrast optical micrographs and the corresponding 2D-FFT power spectra of PSA/PVME (30/70) blends photo-cross-linked at 105 °C over 40 min. Irradiation with linearly polarized light along the Y direction as indicated by the arrow: (a) phase-contrast optical micrograph; (c) 2D-FFT power spectra. Irradiation with unpolarized light: (b) optical micrograph; (d) 2D-FFT power spectra. The scales are 10 μm for the micrographs and 3×10^4 cm^{-1} for the power spectra.

the irradiated sample ($8\times8\times0.05$ mm) far away from the interfaces between the mixtures and the two glass substrates. The thickness 50 μm was chosen in order to minimize the gradient of the exciting light in the samples and also to avoid the wetting effects which might take place within 10 μm from the surfaces of the glass substrates [13]. The phase separation kinetics was obtained by monitoring the time evolution of the morphology emerging at the same position of the blend over various irradiation times. The characteristic length scales of the morphologies obtained under different experimental conditions were obtained by sector-averaging the two-dimensional power spectra of the corresponding optical micrographs by fast Fourier transform (FFT).

Upon irradiation with linearly polarized light, anthracenes labeled on PSA chains are selectively excited and undergo photodimerization as soon as an excited anthracene encounters another unexcited one in the mixture. As a result, the photodimers, i.e., the product of the reaction, form cross-linking junctions between PSA chains and thus destabilize the reacting mixture by the network formation. This reaction is known to be irreversible below 200 °C [14]. Due to this photoselection, the orientational distribution of these cross-linking junctions is not randomly generated but is formed with the probability given by $P(\theta)\propto\cos^2\theta$ [15]. Here, θ is the angle between the electric field **E** of the polarized light and the absorption transition moment ($\boldsymbol{\mu}$) of anthracene. As a consequence, the unstable modes determining the morphology of the irradiated blend become polarization selective.

As illustrated in Fig. 2(a) as an example, a PSA/PVME (30/70) blend photo-cross-linked by irradiation with linearly polarized light (**E**) parallel to the Y axis at 105 °C exhibits a lamellalike structure on the micrometer scales with the orientation closely *perpendicular* to (**E**). To confirm the effects of linearly polarized light on the phase separation, a PSA/PVME (30/70) mixture was irradiated under the same conditions except that the polarization (**E**) was set parallel to the Z axis. The mixture undergoes phase separation under this particular cross-linking condition and exhibits lamellar structures again closely perpendicular to the polarization (**E**). Moreover, as shown in Fig. 2(b), in contrast with these results, a PSA/PVME (30/70) mixture exhibits isotropic interconnecting (spinodal) structures upon irradiation with *unpolarized* light of the same intensity. The anisotropy of the morphology revealed by the 2D-FFT power spectra in Fig. 2(c) clearly indicates that the concentration fluctuations arising from the cross-linking reaction were selectively frozen by the linearly polarized light.

There are mainly two factors affecting the direction of the lamella shown in Fig. 2(a). One is the selection efficiency of the reaction and the other is the reorientational relaxation of PSA segments after cross-linking. There is also another important factor that is the gradient of the cross-linking densities generated by the orientational distribution of the reaction. Consequently, an elastic strain field might gradually develop and act as a long-range interaction in the reacting mixture, inducing the couplings between the local reaction and the concentration fluctuations. It is worth noting that the morphological anisotropy illustrated in Fig. 2 becomes insignificant when the cross-linking reaction is performed at temperatures higher than 110 °C, whereas the phase separation does not occur when cross linking was carried out at temperatures below 50 °C.

In general, the orientation of the lamellae is not completely perpendicular to the polarization **E**. As shown in Fig. 2(c), the 2D-FFT power spectra of these structures initially exhibit strong diffraction spots along the Y-axis direction. These patterns gradually shift toward the side of lower frequencies while becoming broader as irradiation time increases. This time-evolution process corresponds to the coarsening and disordering of these lamellar structures, which are initially oriented along the Z axis in the early stage of phase separation. In order to quantitatively examine this particular kinetics, the characteristic lengths ξ of the structures corresponding to the diffraction pattern at a given angle θ with respect to the polarization **E** were calculated by using the Bragg formula $\xi(\theta)=2\pi/q_m(\theta)$, where $q_m(\theta)$ is the frequency corresponding the maximum intensity of the 2D power spectra in the direction θ. For all the orientation, the growing process of ξ can be well described by the Liftshitz-Slyozov-Wagner (LSW)-like law $\xi\propto t^{\alpha}$ [16,17], where the exponent α can be used as a measure of the growth process. Shown in Fig. 3(a) is the time evolution of the characteristic length scales ξ obtained at three different orientations: 45°, 100°, and 155° with respect to the polarization **E**. It was found that within the time scale of these experiments (300 min), the exponent α largely changes with the orientation θ. Among these three orientations, the exponent α is smallest (0.076) at 155°, whereas it is largest (0.19) for $\theta=100°$, indicating that α decreases gradually with increasing $\cos^2\theta$, the probability of the cross-linking reaction induced by polarized light. In other words, the phase separation was more suppressed in the direction of high cross-linking densities. Since the reaction rate $k(\theta)$ at a given orientation θ is proportional to the probability $\cos^2\theta$, the characteristic length scale $\xi(t)$ shown in Fig. 3(a) was replotted versus the prod-

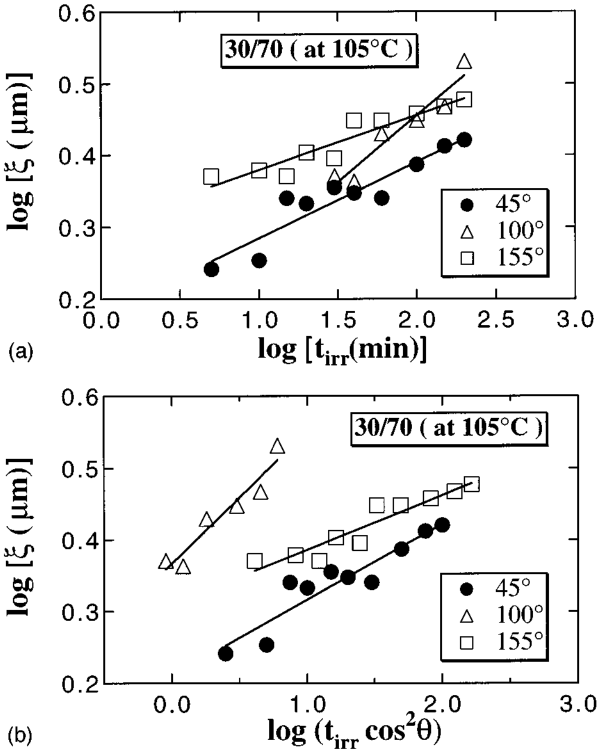

FIG. 3. (a) Phase separation kinetics of a PSA/PVME (30/70) mixture irradiated at 105 °C with linearly polarized light along three orientations with respect to the exciting polarization (**E**):45°, 100°, and 155°; (b) the reduced plot of (a) with the reaction time rescaled by the factor $\cos^2\theta$.

uct of irradiation time t_{irr} and $\cos^2\theta$ in Fig. 3(b) in order to compensate for the dependence of the cross-linking reaction rate k on θ. On the other hand, the dependence of the exponent α on the orientation θ with respect to the direction of the exciting polarization **E** is illustrated in Fig. 4. It can be seen from these results that α increases with θ and reaches its maximum magnitude in the vicinity of θ=90°–100° before decreasing with further increase in θ. Furthermore, the phase separation proceeds most slowly along the direction parallel to (**E**) with the exponent $\alpha = 0.06$, and most quickly in the perpendicular direction with $\alpha = 0.19$. These data clearly indicate that the phase separation kinetics of PSA/PVME (30/70) blends reflects the selectivity of the reaction determined by the factor $\cos^2\theta$. It is also worth noting that there exists a time delay in the phase separation observed at different orientations, as illustrated by different symbols in Fig. 4. In principle, the ordinate of Fig. 3 can be also rescaled by using some appropriate length scales such as the reciprocal of the critical wave number $q_c(\theta)$ in the initial stage (linear region) of the phase separation obtained at a given orientation by light scattering. However, these data are currently not available because the light scattering patterns are often distorted by the spatial inhomogeneity produced by the reaction in the cross-linked samples. Nevertheless the strong dependence of the kinetic exponent α on the orientation θ might be a signature of the interference between unstable modes propagating with different rates along different orientations in the blend under irradiation with linearly polarized light.

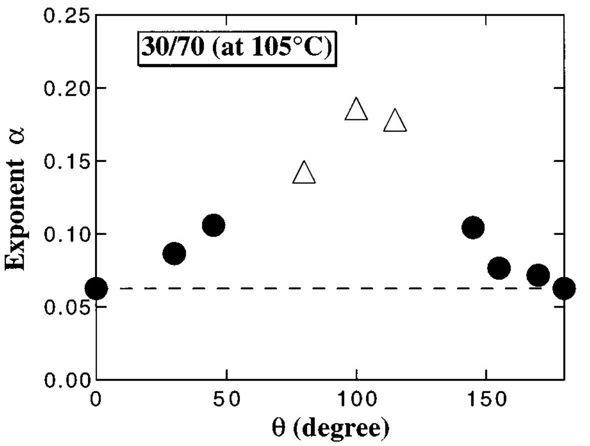

FIG. 4. Dependence of the kinetic exponent α on the orientation θ obtained for a PSA/PVME (30/70) mixture photo-cross-linked with linearly polarized light. The time delay of the phase separation occurring at different orientations is expressed by different symbols: emerging at 5 min (●) and at 30 min (△) after irradiation.

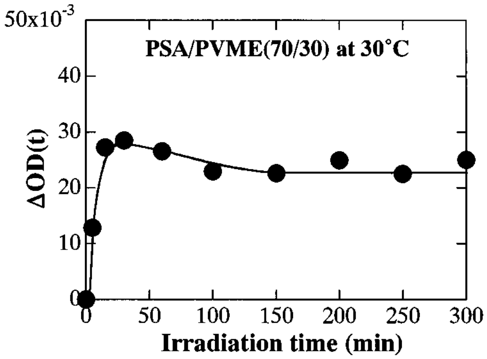

FIG. 5. Irradiation time dependence of the dichroism of the *unreacted* anthracenes labeled on PSA chains in a PSA/PVME (70/30) mixture irradiated with linearly polarized light at 30 °C.

In order to confirm the selectivity of the reaction induced by polarized light, the two dichroic components $OD_{\parallel}(t)$ and $OD_{\perp}(t)$ of the *unreacted* anthracenes were monitored respectively in the directions parallel and perpendicular to the polarization (**E**) for a PSA/PVME (70/30) blend photo-cross-linked at 30 °C in the miscible region. It was found that $OD_{\perp}(t)$ is always larger than $OD_{\parallel}(t)$, revealing the selectivity of the cross-linking reactions. This selection becomes more obvious when the dichroism $\Delta OD(t) = [OD_{\perp}(t) - OD_{\parallel}(t)]$ was plotted versus irradiation time in Fig. 5. It was found that in the early stage, the dichroism $\Delta OD(t)$ increases with irradiation time and approaches a constant value after passing through a maximum at ca. 30 min after irradiation. This selection resembles the behavior of polarization-selective photochemical reactions reported previously for the cagelike molecule cyclophane in the glassy state of poly(methyl methacrylate) [18]. The temporal behavior of this dichroism can be explained by using the model of rotational diffusion-controlled reaction proposed recently for the mechanism of polarization-selective reactions in liquids [19]. From the results described above, it can be concluded that the symmetry breaking of concentration fluctuations observed in this work is the consequence of the selectivity of the cross-linking reaction induced by linearly polarized light.

Currently, though the exact mechanism of this symmetry-breaking process is not completely understood, it is highly possible that the effects of the elastic stress associated with the preferential contraction of the PSA networks in the irradiated mixtures along the polarization direction might play a key role in the formation of these lamellar structures. The polarization-induced ordering phenomena described in this work not only give insights into the development of another method for morphology control of polymer materials but also provide a physico-chemical system to investigate the mode-selection processes for the phase separation taking place under inhomogeneous conditions.

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