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Phase Separation of Polymer Mixtures Induced by Polarization-Selective Chemical Reactions: Spatial Symmetry Breaking and Mode Selection

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SUMMARY: Phase separation of polystyrene / poly (vinyl methyl ether) (PS/PVME) blends was induced and controlled by irradiation with linearly polarized light. The PS component was made photosensitive by chemically labeled with either anthracene or *trans*- stilbene. The former was used to cross-link the PS component whereas the latter induces phase separation by changing polymer segmental volumes. The phase separation and reaction kinetics were observed and discussed in terms of mode-selection process.

Introduction

A binary mixture undergoes phase separation as soon as it is brought from the homogeneous one-phase into the two-phase regions. Depending upon the experimental conditions, a wide variety of morphology can emerge from this phase separation process [1)]. For most cases, phase separation has been considered as a spatially uniform phenomenon under translationally and rotationally invariant conditions. However, in practice, spatial inhomogeneity is often accompanied with phase separation as encountered in polymer processing or directional solidification of binary liquids and metallic alloys [2, 3)] where phase separation becomes a spatially dependent phenomena. In order to understand the time-evolution of these dynamical processes in polymers, we have observed phase separation in the presence of a gradient of temperature [4, 5)] as well as light intensity [6)]. It was found in these experiments that, when the condition *translationally invariant* does not hold, there exists an interference process between the thermodynamic instabilities arising at a given position and those developing with different rates in its neighbor along the gradient in the mixture. Here, we report the phase separation of binary polymer mixtures driven by irradiation with linearly polarized light. The thermodynamic destabilization of polymer mixtures by polarization-selective photochemical reactions [7)] gives rise to the orientation-dependent phase separation in which the condition *rotationally invariant* is no longer valid. By combining the reaction data with the phase separation kinetics and by analyzing the morphology resulting from cross-linking as well as

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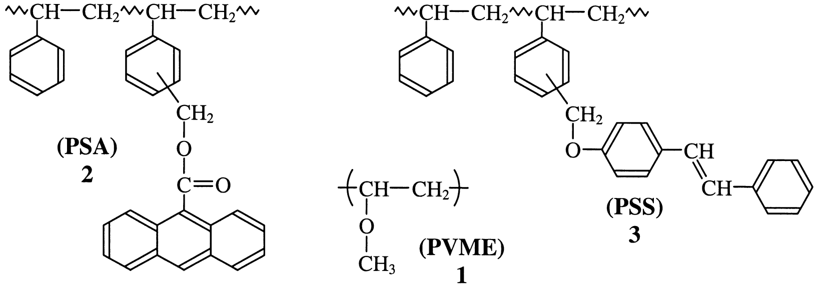
non-cross-linking reactions, the mechanism of these mode-selection processes are examined and discussed.

Samples and Data Analysis

Samples used in this study are polystyrene (PS)/poly(vinyl methyl ether) (PVME, **1**) mixtures. To induce phase separation with linearly polarized light, polystyrene was labeled with either anthracene (PSA, **2**) or *trans*- stilbene (PSS, **3**). It was known that both PSA/PVME and

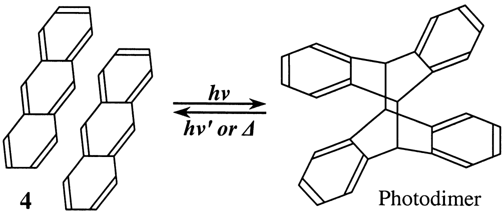


(PSA) **2**

(PVME) **1**

(PSS) **3**

PSS/PVME mixtures possess a lower critical solution temperature (LCST)[8, 9]. Anthracene (**4**) and stilbene (**5**) have the well-defined absorption dipole moments so that they can be selectively excited with linearly polarized light. Upon irradiation with linearly polarized light (**E**), PSA networks are formed due to photodimerization of anthracene, whereas the segmental volumes of PSS and its enthalpic interactions with PVME segments increase due to the *trans cis* photoisomerization of stilbene[10]. Both the chemical transformation leads to phase separation of the mixtures. The morphology resulting from these reactions was observed by phase-contrast optical microscopy and was analyzed by 2-dimensional fast Fourier Transform (2D-FFT). The detailed analysis was described elsewhere[11]. The intensity of UV-light (365 and 313nm) from a Hg-Xe was fixed at 3.0 mW/cm^2.



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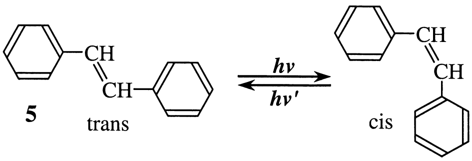

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Mode selection in phase separation induced by photo-cross-link

Upon irradiation with linearly polarized light, anthracene in PSA/PVME blends was selectively photodimerized, leading to anisotropic phase separation. As an example, the morphology of a PSA / PVME (30/70) blend irradiated with linearly polarized light (365 nm) at 105 °C is shown in Figure 1a. The lamella-like structure appears in the direction almost perpendicular to the polarization (**E**). In contrast to this result, the morphology irradiated with *unpolarized* light shown in Fig. 1b is isotropic under the same conditions. These results suggest that the unstable modes developing along the direction parallel to the polarization (**E**) were frozen due to the high selectivity of the reaction. It should be noted that the probability of the reaction at an orientation θ with respect to the polarization (**E**) is proportional to $\cos^2 \theta$. The orientational dependence of the phase separation kinetics was obtained from the time-evolution of the characteristic length scale ξ of the morphology calculated from the 2D power spectra. An example is shown in Figure 2 for a PSA / PVME (30/70) blend irradiated at 105 °C. In accordance with the orientational dependence of the cross-linking density, phase separation proceeds fastest along the direction perpendicular to (**E**), whereas it is much slower in the direction parallel to (**E**). Furthermore, unlike the case of irradiation with *unpolarized* light, phase separation kinetics obtained with polarized light cannot be expressed by a master curve when ξ is plotted versus the reduced time ($t_{irr} \times \cos^2\theta$) in logarithmic scale as shown in Figure 2. These results imply that phase separation induced by linearly polarized light does not only depend on the light intensity, i.e. on the reaction rate, but it is also strongly affected by the

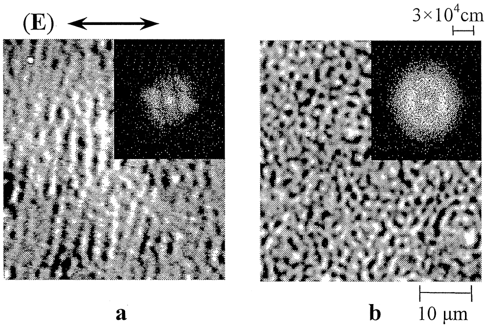

Fig. 1. Phase-contrast optical micrograph and 2D-FFT power spectra of a PSA/PVME (30/70) blend irradiated with linearly polarized light over 40min at 105 °C.

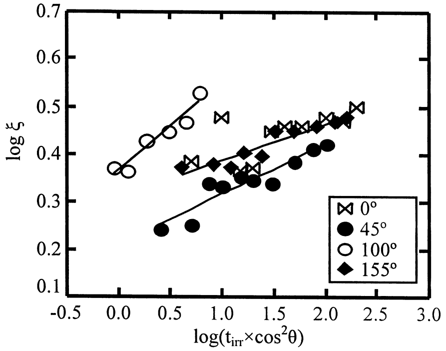

Fig. 2. Reduced plot of the characteristic length scales at different orientations at 105 °C.

interference between instabilities propagating with different rates along different orientations in the sample.

Mode selection in phase separation induced by photoisomerization

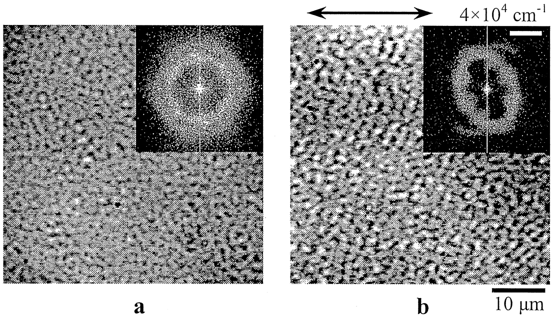

Fig. 3. Morphology and the corresponding power spectra of a PSS/PVME (20/80) blend irradiated with *unpolarized* (a) and *polarized light* (b) at 90 °C.

In order to gain further insight into the anisotropic phase separation directed by linearly polarized light, photoisomerization was utilized instead of photo-cross-link. The feature of photoisomerization is that it does not greatly modify the mobility of polymer chains in the blend. Illustrated in Figures 3 is the morphology of a PSS / PVME (20/80) blend induced by photoisomerization using linearly polarized light at 90 °C. In contrast to the case of unpolarized light, the resulting morphology was anisotropic. Compared to the case of photo-cross-link using anthracene as shown in Fig. 1, the morphological anisotropy obtained with *trans* → *cis* photoisomerization is much weaker as revealed by the elliptic power spectra depicted in the inset of Fig. 3b. It is worth noting that this anisotropy almost disappears at temperatures higher than 105 °C, which is 10 °C above the glass transition temperature Tg of the PSS component. The time-evolution of the anisotropic phase separation observed for a PSS / PVME (20/80) blend was examined by monitoring the irradiation-time dependence of the 2-dimensional power spectra of the corresponding morphology. To quantify the morphological anisotropy, the ratio D of the long to the short axes of the elliptic power spectra of the morphology was defined and used as a measure for the anisotropy of phase separation:

$$D(t) = \frac{q_1(t)}{q_s(t)} \qquad (1)$$

where $q_1(t)$ and $q_s(t)$ are respectively the wave-numbers corresponding to the long and short axes of the 2D-power spectra. Physically, $D(t)$ expresses the characteristic ratio of the two morphological periodicities along the directions parallel and perpendicular to the exciting polarized light. Shown in Figure 4 is the irradiation time dependence of the characteristic ratio

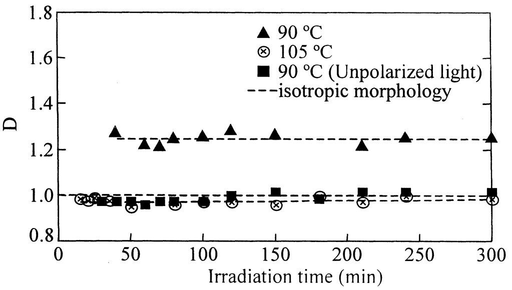

Fig. 4. Irradiation-time dependence of the characteristic ratio $D(t)$ observed at various temperatures for a PSS / PVME mixture.

$D(t)$ obtained for PSS / PVME (20/80) under several irradiation conditions. At 90 °C, which is located at 5 °C below Tg of the PSS component, the characteric ratio $D(t)$ was a constant and almost unchanged with irradiation time. On the other hand, the magnitude of $D(t)$ obtained at 105 °C is almost equal to unity and is indistinguishable from the value obtained by irradiation with *unpolarized* light. These results indicate that the spatial distribution of the photoisomerization generated by linearly polarized light in the blend was not permanently sustained and relax to the isotropic state upon irradiation at high temperatures. In the case of photo-cross-link, the temperature at which this morphological anisotropy becomes weakened and almost vanishes is above 130 °C. These data suggest that far below Tg of both PSS and PSA, the spatial distribution of the photochemical reactions induced by linearly polarized light in these blends can be frozen by the development of the PSS-rich or the cross-linked PSA domains during the phase separation process. For temperatures far above Tg of PSS and PSA, this spatial distribution relaxes during the phase separation process. The reaction anisotropy revealed by the photodimerization and photoisomerization kinetics monitored in the one-phase region of these two blends is illustrated in Figure 5. Here, the dichroism of the reaction, which is defined as:

$$\Delta OD(t) = \frac{\left| OD_{\perp}(t) - OD_{\parallel}(t) \right|}{OD_0}$$

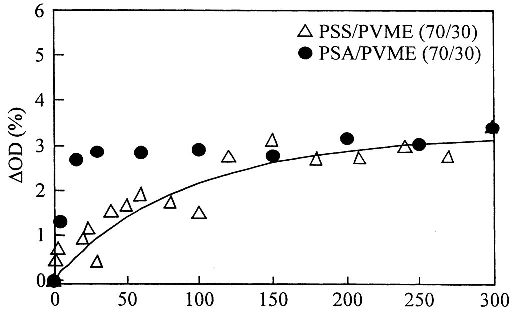

Fig. 5. Dichroic absorbance of a PSA/PVME and a PSS/PVME blend obtained at 105 °C and 90 °C, respectively.

was plotted versus irradiation time. OD_0, $OD_{\perp}(t)$ and $OD_{\parallel}(t)$ are respectively the initial absorbance and the absorbance of anthracene or *trans-* stilbene measured in the directions perpendicular and parallel to the polarization (**E**). Under similar experimental conditions, the dichroism of anthracene builds up quickly within 40 min and tends to approach a stationary state. On the other hand, the dichroism of *trans-* stilbene increases slowly with irradiation time and does not yet reach the equilibrium within the experimental time scale. These reaction kinetic data are in agreement with the morphological results illustrated in Figs. 1 and 3, indicating that anisotropy of phase separation induced by the cross-linking reaction is much stronger than the case of photoisomerization. This difference can be explained by the fact that polymer diffusion is directly frozen by the cross-linking reaction, whereas it is only indirectly suppressed by the increase in PSS-rich domains during the course of phase separation induced by photoisomerization.

Concluding Remarks

By using polarization-selective chemical reactions, we have demonstrated that the spatial symmetry of concentration fluctuations in binary polymer mixtures can be broken, leading to anisotropic phase separation. This selectivity of chemical reactions generates a mode-selection process in the phase separation of polymer mixtures. The findings can be summarized as follows:

1) The spatial distribution of photodimerization and photoisomerization induced by linearly polarized light generates anisotropic fluctuations in PSA/PVME and PSS/PVME blends. During the phase separation, these fluctuations couple with elastic strain originated by the reaction distribution, giving rise to the long-range anisotropy.
2) These concentration fluctuations with broken symmetry are frozen either by the decrease in mobility caused by the network formation for the case of PSA or by the glassification of the domains rich in PSS during the course of phase separation. This freezing of fluctuations is the origin of the anisotropic phase separation.
3) Polymer mixtures irradiated with polarized light can exhibit multicriticality because of the spatial distribution of the reactions. There also exists the interference processes of thermodynamic instabilities propagating with different rates along different orientations. Thus, polymer mixtures irradiated with polarized light can provide a model system to study the mode-selection processes in condensed matter.

Acknowledgements

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