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Directional Phase Separation of Binary Polymer Blends Driven by Photo-Cross-Linking with Linearly Polarized Light

Katsunari Kataoka,[†] Osamu Urakawa,[‡] Hiroya Nishioka, and Qui Tran-Cong*

Department of Polymer Science and Engineering, Kyoto Institute of Technology, Matsugasaki, Kyoto 606-8585, Japan

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ABSTRACT: Phase separation of anthracene-labeled polystyrene/poly(vinyl methyl ether) (PSA/PVME) blends was induced by photo-cross-linking the PSA chains with linearly polarized light in the one-phase region of the blend. The cross-linking reaction was performed by taking advantage of the polarization-selective photodimerization of anthracene labeled on the PSA chains. Under this particular irradiation condition, the spatial symmetry of concentration fluctuations was broken, resulting in anisotropic phase separation directed by the exciting polarization. By comparison of these experimental data with those obtained by using *unpolarized* light under the same conditions, it was found that the morphology induced by linearly polarized light reflects the interference between instabilities propagating with different rates along different directions in the reacting blends.

I. Introduction

Phase separation of polymer blends accompanied by chemical reactions, particularly with cross-links, is not only related to practical aspects such as curing of polymers[1] but also belongs to a universal class of pattern formation processes where the so-called modulated phases arise because of the competition between two or more antagonistic interactions.[2] It has been shown from the analytical as well as numerical calculations of the time-dependent Ginzburg−Landau (TDGL) equation that the long-wavelength fluctuations in a binary mixture undergoing phase separation can be suppressed in the presence of reversible reactions.[3−6] Recently, these soft-mode suppression phenomena have been experimentally observed in the phase separation of binary blends accompanied by photoisomerization.[7] Freezing of these soft modes was also reported previously in the in situ photo-cross-links of polymer blends during the spinodal decomposition process[8] and inside the miscible region of polymer blends[9] where the polymer mobilities are suppressed by the cross-linking reactions. This soft-modes suppression leads to the spontaneous pinning of phase separation during the chemical reaction.

In practice, phase separation of polymers often takes place under physically as well as chemically *nonuniform* conditions because temperature gradients or inhomogeneous reactions are frequently encountered in large-scale experiments. As a first step toward the understanding of the phase-separation phenomena resulting from thermodynamically nonuniform conditions, we examine in this work the kinetics and the morphology of anthracene-labeled polystyrene/poly(vinyl methyl ether) (PSA/PVME) blends undergoing phase separation directed by cross-linking with linearly polarized light. The reaction was performed by taking advantage of the polarization-selective photodimerization of anthracene[10,11] chemically labeled on the PSA chains. Because of the selectivity of the reaction in the blend, the cross-linking densities of PSA chains are predominantly generated along the direction of the exciting polarization (**E**). As a result, the mixture is preferentially stabilized or destabilized along the direction of (**E**), depending upon the quench depth.

In a previous communication, we have reported the preliminary results of the phase separation driven by irradiation with linearly polarized light in a binary polymer blend PSA/PVME.[12] In this paper, the detailed experimental data are reported together with the discussion on the possible mechanism of the phenomena. First, the kinetics of the phase separation directed by linearly polarized light was described. Subsequently, the selectivity of the cross-linking reaction was confirmed by monitoring the irradiation time dependence of the dichroic absorption of the anthracene moieties labeled on the PSA chains. Small-angle X-ray scattering was also used to observe the anisotropic fluctuations developing in the blend under irradiation with polarized light. The mechanism of this directional phase separation was examined and discussed by following the dependence of the phase separation and the reaction kinetics on the blend composition. Finally, the evidence for the interference between the concentration fluctuations propagating with different rates along different orientations in the blend is discussed by comparing the kinetic data of phase separation induced by polarized and unpolarized light under the same conditions.

II. Experimental Section

1. Samples. Anthracene-labeled polystyrene/poly(vinyl methyl ether) (PSA/ PVME) mixtures were used as samples. PSA ($M_w = 3.2 \times 10^5$, $M_w/M_n = 1.7$) was prepared according to the synthesis procedure described previously.[13] The label content of the polymer is 1 anthracene/40 monomer units of the PSA chains. The chemical structure of the polymers used in this work is illustrated in Figure 1. Poly(vinyl methyl ether) (Aldrich, $M_w = 9.5 \times 10^4$, $M_w/M_n = 2.2$) was purified twice by using methanol/*n*-heptane mixtures. All the samples were prepared by casting toluene solutions containing PSA and PVME blends of appropriate compositions. PSA/PVME blends were carefully dried under vacuum to remove solvent and were sandwiched between the two quartz plates with a 50-μm

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* To whom correspondence should be addressed.

[†] Current address: Dai Nippon Printing Co. Ltd., Kyoto, Japan.

[‡] Current address: Department of Macromolecular Science, Graduate School of Science, Osaka University, Osaka 560-0043, Japan.

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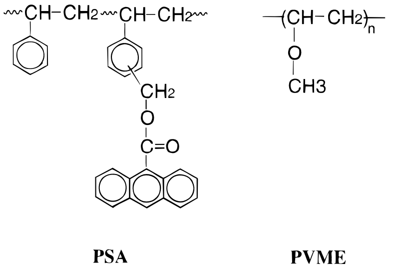

Figure 1. Chemical structures of the anthracene-labeled polystyrene (PSA) and poly(vinyl methyl ether) (PVME).

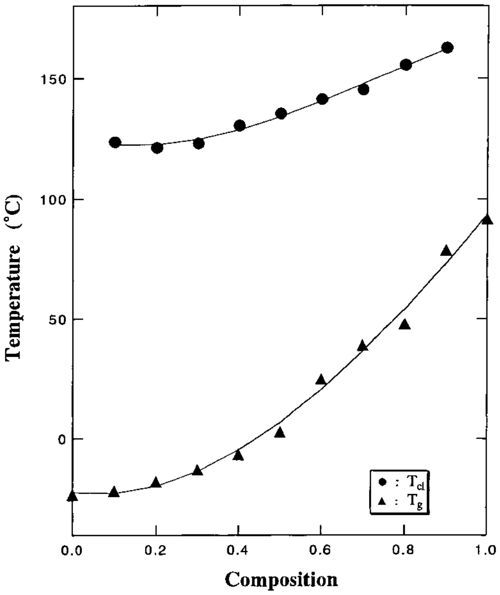

Figure 2. The cloud points T_{cl} (●) and the glass-transition temperature T_g(▲) of PSA/PVME blends measured respectively by light scattering and differential scanning calorimetry (DSC).

aluminum spacer used to adjust the sample thickness. The details of the blend preparation were described elsewhere.[13]

2. Irradiation Experiments. A photo-cross-linking reaction of PSA chains was induced and controlled via photodimerization of anthracene by using a mercury−xenon (Hg−Xe) lamp (500 W, Hamamatsu Photonics). The ultraviolet (UV) light from the Hg−Xe lamp was converted into linearly polarized light of appropriate wavelengths by passing it through a polarizer (HNBP′, Polaroid Inc.) and a sharp-cut optical filter (SC-052, Corning Inc.). The intensity at the excitation wavelength, 365 nm, was adjusted at 3 mW/cm^2 for all the experiments described in this work. Upon excitation with linearly polarized light (**E**), anthracene selectively undergoes photodimerization with the probability $\cos^2 \theta$ where θ is the angle between the polarization (**E**) and the absorption transition moment of anthracene.[10] This photoselection introduces into the sample a preferential direction for the cross-linking reaction and thus generates a spatial distribution of cross-linking densities in the blend during irradiation.

3. Cloud Points and Glass-Transition Temperatures of the Blends. The cloud points (T_{cl}) of the blends were measured by light scattering at a fixed angle under three heating rates: 0.5, 0.2, and 0.1 °C/min, and were linearly extrapolated to zero-heating rates in order to minimize the kinetic effects arising from the slow diffusion of polymer chains. The glass-transition temperatures (T_g) of PSA/PVME blends were measured by using differential scanning calorimetry (Mac Science, model 3100) with the heating rate at 5 °C/min. Figure 2 shows the cloud points and the glass-transition temperatures of PSA/PVME blends obtained under the experimental conditions described above.

4. Observation and Analysis of the Blend Morphology. The morphology of the irradiated blends was observed by using a phase-contrast optical microscope (Nikon, model XF-NTF-21). The optical images were digitized by using an image analyzer (Pias, LA-525, Japan) and the data were subsequently transferred to a computer (Macintosh, 7100/80AV) where further analysis using two-dimensional fast Fourier transform (2D-FFT) of the digitized images was performed by using standard software. To increase the signal/noise ratio of the one-dimensional (1D) power spectra, the circular and sector averages of the 2D power spectra were carried out respectively for isotropic and anisotropic morphologies. Finally, the characteristic length scale ξ of the structures was calculated from the Bragg condition $\xi = (2\pi/q_{\max})$ where $q_{\max}$ is the frequency corresponding to the maximum of the power spectra.

5. Small-Angle X-ray Scattering (SAXS) Experiments. The small-angle X-ray scattering experiments using synchrotron radiation were carried out at the Photon Factory of the National Laboratoty for High Energy Physics, Tsukuba, Japan. The details of the experiments were described in the previous works.[8] Since the scattering intensity was detected by a one-dimensional position-sensitive proportional counter (PSPC), the scattering profiles at a given temperature of PSA/PVME blends cross-linked with linearly polarized light were measured in the directions parallel and perpendicular to the exciting light by rotating the irradiated blend with respect to the direction of the polarization (**E**).

6. Photo-Cross-Linking Reaction Kinetics. The cross-linking reaction kinetics of PSA chains in the blend under irradiation with UV−light was monitored by using a UV−visible photospectrometer (Shimadzu, UV160). The changes in the absorbance of anthracene with the irradiation time were monitored at 405 nm. The dichroic absorption $\Delta OD(t)$ defined below was used to evaluate the anisotropy of the reaction:

$$\Delta OD(t) = [OD_{\perp}(t) - OD_{\parallel}(t)] \tag{1}$$

Here, $OD_{\perp}(t)$ and $OD_{\parallel}(t)$ are respectively the absorbances of anthracene observed in the directions perpendicular and parallel to the polarization (**E**). The details of measurements and theoretical analysis of the polarization-selective photochemical reactions in polymer solids are described elsewhere.[10−11]

III. Results and Discussion

1. Directional Phase-Separation Kinetics of PSA/PVME Blends Irradiated with Linearly Polarized Light.

A PSA/PVME (30/70) blend undergoes phase separation upon irradiation with linearly polarized light in the one-phase region at 105 °C. The phase separation becomes observable under a phase-contrast optical microscope after 15 min of irradiation and strongly depends on the direction with respect to the polarization (**E**) of the exciting light. The lamella-like morphology observed for a PSA/PVME (30/70) blend after 30, 60, and 100 min of irradiation is shown in Figures 3a. It was found that the direction of these lamellae is almost perpendicular to the electric field (**E**) of the polarized light. As revealed by the corresponding 2D-FFT power spectra shown in the insets of these images, these morphological data are significantly different from the isotropic structures depicted in Figure 3b obtained by cross-linking with *unpolarized* light under the same conditions. It is worthwhile to note that when the direction of the polarization (**E**) is rotated, the orientation of these lamella-like structures changes in such a way that their direction is always closely perpendicular to the exciting polarization (**E**). These results imply that the anisotropy of the morphology observed in Figure 3a is a unique phenomenon arising from the polarization-selective cross-linking reaction. These data also suggest that the spatial symmetry of

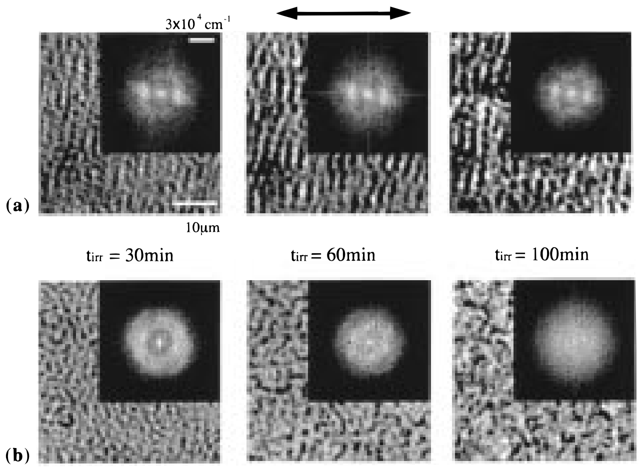

Figure 3. Morphology of a PSA/PVME(30/70) blend obtained after 30, 60, and 100 min of irradiation with linearly polarized light (a) and with unpolarized light (b). Shown in the inset are the corresponding 2D-FFT power spectra. The experimental temperature is 105 °C and the light intensity is 3.0 mW/cm^2 for both cases. The arrow indicates the direction of the linearly polarized light. Here, t_{irr} is the irradiation time.

the concentration fluctuations in the blend was broken by the polarized light. For linearly polarized light incident horizontally (along the x-axis) onto the sample, these lamellae are well-oriented in the early stage as revealed by the strong diffraction spots in the x-axis. As the irradiation time increases, these lamellae become coarsened and their orientation tends to be randomized as seen in Figure 3a for the blend irradiated over 100 min. Neverthless, the diffraction spots appearing in the early stage of irradiation still remain due to the contribution of the structures selectively frozen at the early stage of the reaction. The coarsening process of the phase-separated structures can be observed through the 2D power spectra which become broadened and the peak moves toward lower frequency as the irradiation time increases. As described later in the section of data analysis, together with the results of phase-separation kinetics obtained by irradiation with *unpolarized* light, the data shown in Figure 3 suggest that the phase separation first starts along the direction of the polarization (**E**) and then propagates and interferes with the concentration fluctuations growing slower in other directions.

The phase-separation kinetics of a PSA/PVME (30/70) blend photo-cross-linked by linearly polarized light (**E**) at 105 °C was obtained by analyzing the dependence of the characteristic length scale ξ on the orientation θ with respect to the polarization (**E**). Here, ξ was calculated from the Bragg condition after sector-averaging the 2D-FFT power spectra within a range of 3° for different orientations. As an example, the irradiation time (t_{irr}) dependence of ξ obtained for the three angles 45°, 100°, and 155° is shown in Figure 4 in the double-logarithmic scale. It was found that the phase-separation kinetics of a PSA/PVME (30/70) blend observed at a given orientation θ can be expressed by the following power law:

$$\xi(t) \propto t^{\alpha} \tag{2}$$

where α can be used as an indicator for the growth rate of the phase-separation process.

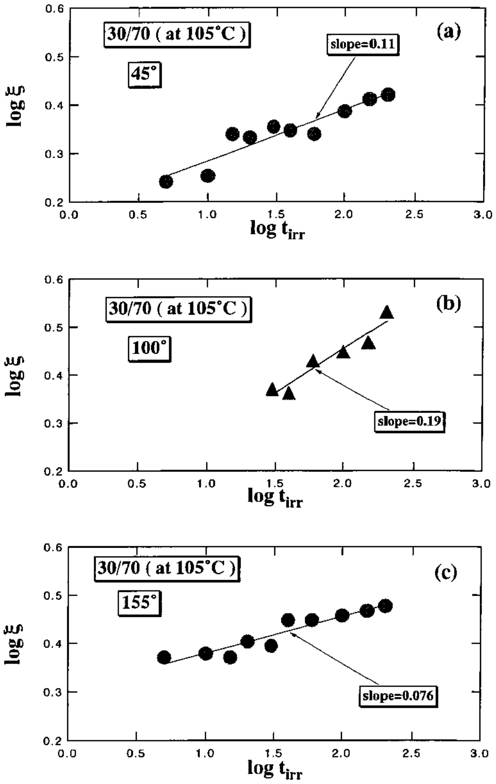

Figure 4. Orientational dependence of phase-separation kinetics obtained for a PSA/PVME (30/70) blend cross-linked by linearly polarized light at 105 °C. The straight lines were obtained by fitting the data to eq 2.

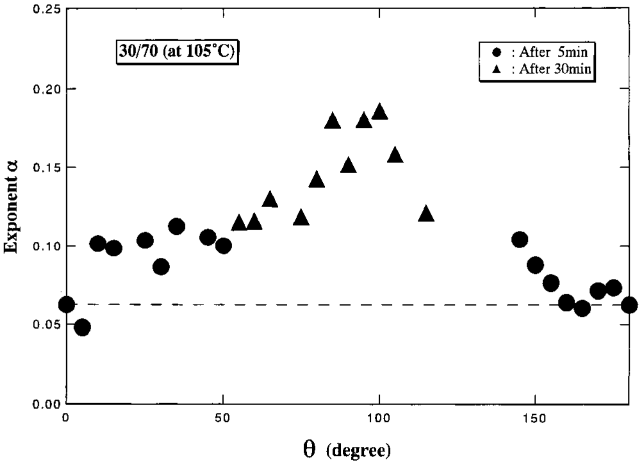

Figure 5. Dependence of the exponent α in eq 2 on the orientation with respect to the polarization (**E**) of the exciting light observed for a PSA/PVME (30/70) blend cross-linked by linearly polarized light at 105 °C. The orientational dependence for the approximate onset of phase separation was indicated by different symbols in the figure.

It is obvious from Figure 4 that the exponent α depends strongly on the orientation θ. The morphological data illustrated in Figure 3a show that the blend was destabilized earlier in the direction parallel to (**E**), reflecting the selectivity of the photodimerization of anthracene upon irradiation with linearly polarized light. Namely, the cross-linking reaction of PSA chains preferentially proceeds along the direction parallel to (**E**) with the probability $P(\theta) = \cos^2 \theta$ where θ is the angle between the absorption dipole of anthracene and the polarization (**E**) of the excitation light.[10] Shown in Figure 5 is the orientation dependence of the exponent α obtained by fitting the experimental data to eq 2. It was found that the phase separation proceeds fastest

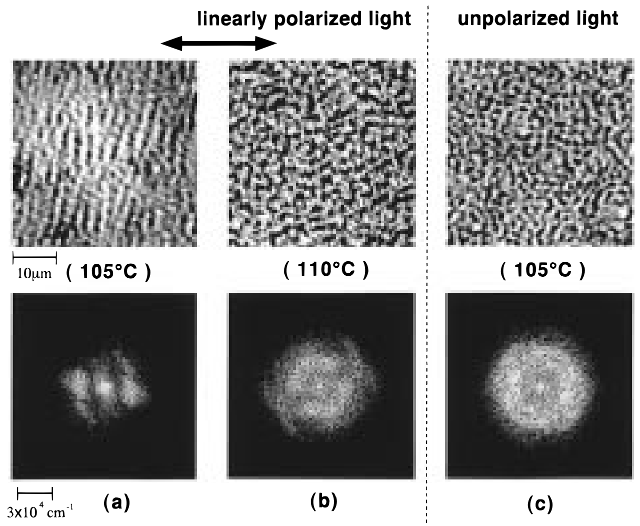

Figure 6. Temperature dependence of the phase separation of PSA/PVME (30/70) blends induced by photo-cross-links: irradiation with linearly polarized light at (a) 105 °C and (b) 110 °C; irradiation with unpolarized light at 105 °C (c). Upper part: phase-contrast optical micrographs. Lower part: the corresponding 2D-FFT power spectra.

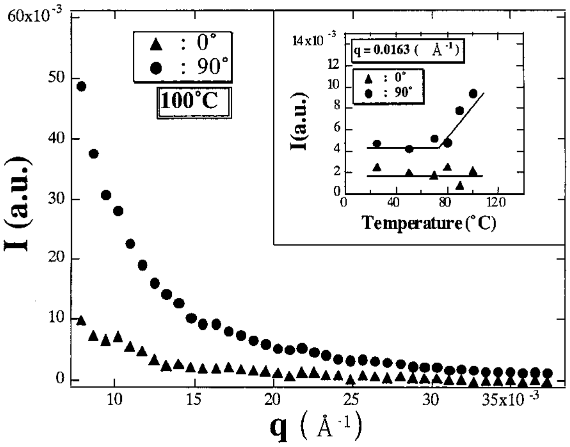

Figure 7. The SAXS profiles of a PSA/PVME (30/70) blend irradiated in 217 min with linearly polarized light observed at 100 °C: (▲) parallel direction; (●) perpendicular direction. Inset: temperature dependence of the SAXS intensity observed at $q = 0.0163$ Å^{-1} in the parallel (▲) and perpendicular (●) directions to the polarization (**E**).

in the vicinity of $\theta = 90°-100°$ with $\alpha \approx 0.2$ whereas it becomes slowest with $\alpha = 0.05$ in the direction parallel to (**E**). Furthermore, the anisotropy of the morphology is almost insignificant at higher temperatures as shown, for example, in Figure 6b for a PSA/PVME (30/70) blend cross-linked in 40 min with linearly polarized light at 110 °C. Though it requires a longer irradiation time for the phase separation to take place, these anisotropic morphologies were also observed at a lower temperature (100 °C). However, the phase separation was not observable by optical microscopy for irradiation temperatures below 70 °C. The strong kinetic effect associated with the high cross-linking densities resulting from irradiation at temperatures far from the phase boundary might be responsible for the phase behavior of the blends photo-cross-linked at low temperatures.[9]

To confirm the existence of the anisotropic concentration fluctuations in the blends cross-linked with polarized light, a PSA/PVME (30/70) blend was irradiated with linearly polarized light over 217 min at 30 °C which is 93.2 °C below the cloud point. It is worth noting that the cross-link density of the PSA chain under this irradiation condition is about 1 cross-link/170 repeat monomer units. This experimental condition corresponds to a "shallow quench" where the phase boundary cannot reach the experimental temperature during irradiation. Subsequently, the temperature dependence of the small-angle X-ray scattering from the cross-linked blend was measured in the directions parallel and perpendicular to the polarization (**E**) of the exciting light. Within the temperature range 25−100 °C, the scattering intensity observed along the parallel direction is always smaller than that in the perpendicular direction, suggesting that the concentration fluctuations are preferentially suppressed along the direction of (**E**) due to the selectivity of the reaction. As an example, the SAXS scattering profiles obtained at 100 °C are shown in Figure 7. For a given magnitude of the scattering vector q, as the temperature increases, the intensity in the parallel direction is almost unchanged while the intensity in the perpendicular direction exhibits the critical scattering behavior as depicted in the inset of Figure 7 for $q = 0.0163$ Å^{-1} taken as an example. This significant difference in the scattering intensities observed for these two directions probably originates from the distribution of cross-linking densities in the sample induced by linearly polarized light as described later in the section of reaction kinetics.

Seemingly, these scattering results are in contrast with the morphological and phase-separation kinetic data shown respectively in Figures 3 and 4. This discrepancy can be explained by the difference in the kinetic effects associated with the cross-linking reactions performed at different quench depths. Namely, when the blend is photo-cross-linked in the region close to T_g, the phase boundary cannot reach the experimental temperature. Under this circumstance, the cross-linking density in the parallel direction is always higher than that in the perpendicular direction as far as irradiation is continued. As a consequence, the concentration fluctuations are preferentially suppressed in the parallel direction. However, upon cross-linking the blend in the region close to the cloud point, the phase boundary can reach the experimental temperature during irradiation when the cross-linking density exceeds a certain threshold. As a result, the blend becomes preferentially unstable along the parallel direction in the early stage of irradiation before the instabities in the perpendicular direction are set in.

2. Kinetics of Photo-Cross-Linking Reactions Induced by Linearly Polarized Light in the One-Phase Region of PSA/PVME Blends. The cross-linking density distribution arising from the spatial selection of the reaction can be clearly observed by following the irradiation time dependence of the dichroic absorption of the cross-linker anthracene at temperatures satisfying the "shallow" quench condition (i.e., far from the phase boundary). Shown in Figure 8 is the irradiation time dependence of the two dichroic absorbance components of anthracene monitored in the directions parallel and perpendicular to (**E**) during the cross-linking process of a PSA/PVME (70/30) blend performed at 30 °C (8.9 °C below its T_g). The component observed along the direction of (**E**) is always smaller than that in the perpendicular direction, experimentally verifying that the cross-linking reaction proceeds preferentially along the direction of the exciting polarization. The dichroism of the reaction calculated from eq

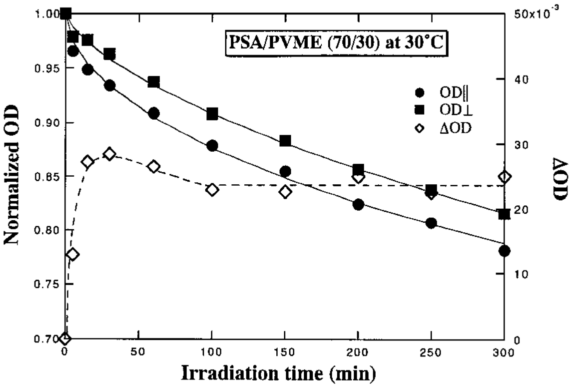

Figure 8. Irradiation time dependence of the two polarized absorption components and the dichroism (Δ*OD*) observed for a PSA/PVME (70/30) blend cross-linked with linearly polarized light at 30 °C.

1 increases with irradiation time in the early stage, then decreases after reaching a maximum at about 40 min, and eventually approaches a stationary value as seen in Figure 8. This particular behavior of the dichroic absorbance can be explained by using the rotational diffusion-controlled reaction model proposed recently.[11] According to this theoretical model, the maximum of the dichroism Δ*OD*(*t*) is determined by the competition between the selectivity of the reaction and the reorientational relaxation of the PSA segments. However, the equilibrium dichroism obtained in the limit of a long irradiation time is controlled by the cross-linking reaction. The correlation between the anisotropy of the cross-linking reactions and the resulting lamellar structures is examined in the next section.

3. Correlation between the Short-Range Polarization-Selective Reaction and the Long-Range Anisotropic Morphologies. The results obtained in Figure 8 indicate that the cross-linking reaction between PSA chains proceeds anisotropically upon irradiation with linearly polarized light. For the lamellar structures to emerge in the micrometer length scale, there might exist a coupling mechanism between the short-range anisotropy of the cross-linking reaction and the long-range orientation of the concentration fluctuations in PSA/PVME blends. To elucidate this mechanism, the kinetics of phase separation as well as the reaction were investigated over a large range of composition. It was found that for a PSA/PVME blend with low PSA compositions (e.g., PSA/PVME (10/90)) cross-linked with 3 mW/cm^2 linearly polarized light at 105 °C, only isotropic morphologies were obtained. As an example, the morphology and the corresponding 2D-FFT power spectra of a PSA/PVME (10/90) blend obtained after 60 min of irradiation with linearly polarized light are shown in Figure 9. Similar results were also obtained with a PSA/PVME (5/95) blend irradiated under the same conditions. These data indicate that the composition of the cross-linkable polymer component in the blends needs to exceed a certain threshold in order to produce lamella-like structures. It is worthwhile to note that the overlap concentration Φ^* of PSA chains in the binary mixture can be estimated by using $\phi^*_{\mathrm{PSA}} \approx N_{\mathrm{PSA}}^{-1/2}$ where N_{PSA} is the polymerization index of the PSA chains.[14] This particular composition is approximately 2 wt %.

As shown in Figure 10, the cross-linking reaction kinetics of the blend with the lowest PSA composition used in this work (PSA/PVME (2/98)) is significantly different from the kinetic data of a PSA/PVME (20/80) blend obtained under the same condition. It was found that the cross-linking reaction in the (2/98) blend proceeds quickly in the early stage of irradiation and is almost terminated at 300 min of irradiation. In contrast to this result, the cross-linking reaction in the PSA/PVME (20/80) blend proceeds slowly under irradiation and still continues after 500 min of irradiation. Both the reaction kinetics of these two blends can be well-described by the sum of two exponential functions of irradiation time:

$$OD(t) = F_{\mathrm{f}} \exp(-k_{\mathrm{f}}t) + F_{\mathrm{s}} \exp(-k_{\mathrm{s}}t) + B \qquad (3)$$

where k_{f} and k_{s} are the rate constants of the fast and slow cross-linking processes, respectively. F_{f} and F_{s} are their corresponding fractions.

B is the baseline introduced into eq 3 to express the fraction of the unreacted anthracene under irradiation. These fitting parameters are summarized in Table 1. It was found that for the blend with low PSA composition (2/98), the fraction of the fast decay process is larger than that of the blend with higher PSA composition (20/80) whereas the reaction rate is almost 3 times larger. Furthermore, the rate of the slow cross-linking process in the (2/98) blend is almost 2 times larger than that of the PSA/PVME (20/80) blend. The fraction of the unreacted anthracenes in PSA/PVME (2/98) is close to 50%.

For photodimerization in bulk polymer matrixes, it has been reported that the reaction proceeds homoge-

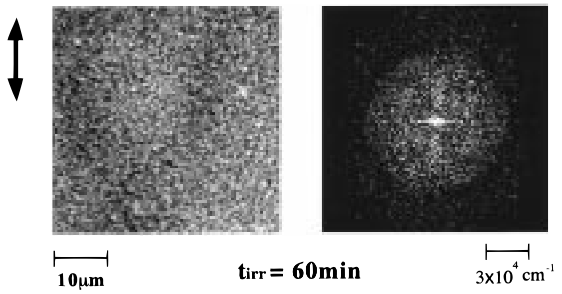

Figure 9. Morphology and the corresponding 2D-FFT power spectra of a PSA/PVME (10/90) blend cross-linked at 105 °C with linearly polarized light propagating along the direction indicated by the arrow. The irradiation time is 60 min and the light intensity is 3.0 mW/cm^2.

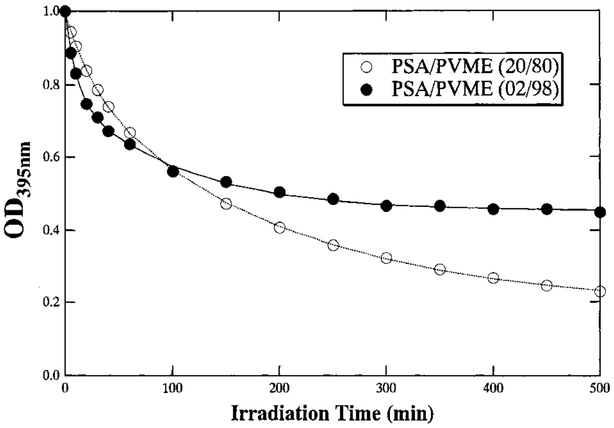

Figure 10. Composition dependence of the photo-cross-linking reaction kinetics observed for PSA/PVME blends irradiated with *unpolarized light* with the intensity 2.0 mW/cm^2 at 30 °C: (●), PSA/PVME (2/98); (○) PSA/PVME (20/80). The sample thickness is 18 μm.

Table 1. Kinetic Parameters of the Photo-Cross-Linking Reactions in PSA/PVME Blends with Different Compositions Obtained by Fitting the Experimental Data to Equation 3 (Excitation Light, Unpolarized Light, 365 nm, 2.0 mW/cm^2; Sample Thickness, 18 μm; Experimental Temperature, 30 °C)

composition (PSA/PVME)	F_f	k_f (min^{-1})	F_s	k_s (min^{-1})	B
(2/98)	0.223	9.91×10^{-2}	0.321	9.67×10^{-3}	0.453
(20/80)	0.193	3.40×10^{-2}	0.620	4.99×10^{-3}	0.181

neously and follows the mean-field kinetics at temperatures above T_g[15] whereas most reactions exhibit the nonhomogeneous kinetics in the glassy region of the matrix.[16,17] Since the intermolecular photodimerization of anthracene is a diffusion-controlled reaction, it can be concluded from the above results that the *intrachain* cross-linking reaction corresponding to the fast process shown in Figure 10 is predominant for the PSA/PVME (2/98) blend at the early stage of irradiation because the probability for the two anthracene molecules on the same PSA chain to encounter each other is much higher than the probability for the *interchain* reactions. However, both the intrachain and the interchain cross-linking reactions take place in the blend with the composition (20/80) upon irradiation because the overlap of PSA chains already takes place in the blend at this particularly high composition of PSA. The cross-linking reaction strongly deviates from the mean-field kinetics in the presence of both the cross-linking processes.[18] The consequence of the inhomogeneity of the reaction induced by linearly polarized light is that, upon irradiation, a spatial distribution of the cross-linking densities is gradually generated in the reacting blends with respect to the direction of the polarization (**E**) as shown in Figure 8. Therefore, a distribution of the elastic modulus might be simultaneously developed in the blend during irradiation. The successive couplings between this orientation-dependent elastic modulus with the concentration fluctuations arising at different irradiation intervals would be the origin of the correlations between the local anisotropy of the reaction and the mesoscopic lamellar structures seen in Figure 3. In general, this coupling is not significant in the blend with low PSA compositions where the intrachain cross-linking reactions are predominant and the forming networks are below the percolation threshold. For this particular case, the orientation distribution of the elastic stress induced by the polarized light can relax during irradiation. That is the case of the isotropic morphologies observed in Figure 9 for a PSA/PVME (10/90) and also in Figure 6 for a (30/70) blend cross-linked at high temperatures (110 °C).

However, when the blends with high PSA compositions are used, both the intrachain and interchain cross-linking reactions take place. As a result, the orientation distribution of the elastic modulus is built-up and is frozen by the cross-linking reaction, leading to a formation of the anisotropic morphologies as shown in Figure 3. The above experimental results imply that the correlation between the anisotropy of the reaction and the mesoscopic lamellar structures is mediated by the elastic stress of the PSA networks.

4. Evidence for the Interference of Instabilities in PSA/PVME Blends Cross-Linked by Linearly Polarized Light. Upon irradiation with linearly polarized light, anthracene moieties labeled on PSA chains are selectively excited and undergo photodimerization with the probability $\cos^2\theta$. As illustrated in Figure 8, this selection introduces into the blend a distribution of cross-linking densities which is highest along the direction of the polarization (**E**) and is lowest in the perpendicular direction. As a consequence, the thermodynamical instabilities of the photo-cross-linked blend might become orientation-dependent. As already seen in Figure 4, phase separation evolves with different rates at different orientations. These experimental data suggest that the morphology of the irradiated blend observed at a given irradiation time and an orientation could be a result of the interference among instabilities propagating along different orientations in the reacting blend. To verify this speculation, PSA/PVME (30/70) blends were irradiated by using *unpolarized* light with various intensities at 105 °C. The phase-separation kinetics observed under these particular irradiation conditions is then compared to the results obtained by linearly polarized light in Figure 4. The comparison is based on the fact that, upon cross-linking with linearly polarized light, the phase separation observed at an arbitrary orientation θ would depend only on the light intensity and consequently follows the same kinetics if the time evolution of the instabilities arising at different directions in the blend are mutually independent. In other words, the phase-separation kinetics under this particular condition is only determined by the reaction rate. Thus, the morphology and its time evolution

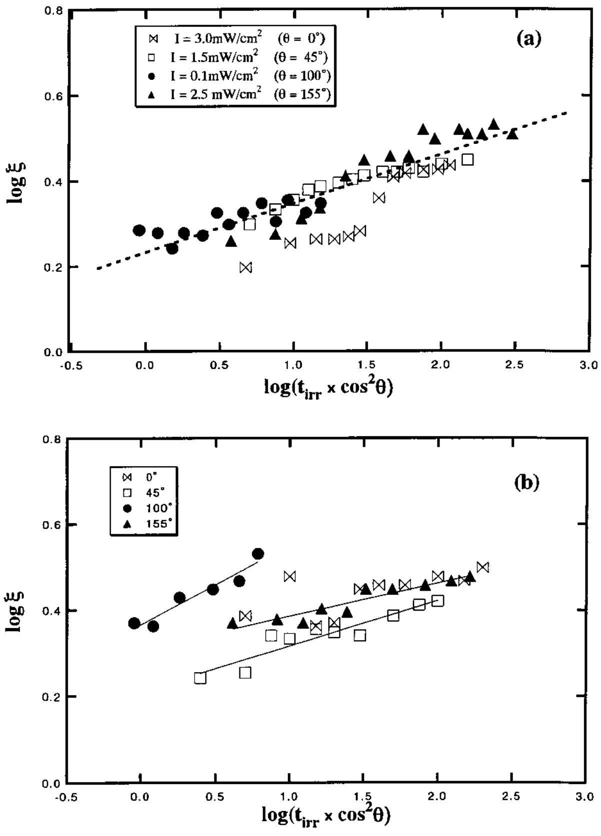

Figure 11. (a) Reduced plot obtained for a PSA/PVME (30/70) blend irradiated with *unpolarized* light. The light intensity was adjusted to be different from 3.0 mW/cm^2 by a factor of ($\cos^2\theta$) as indicated in the inset. The orientations θ at which the blend receives the equivalent irradiation intensity in the case of using linearly polarized light are shown in parentheses in the inset. (b) Reduced plot for the phase separation kinetics observed along the orientation $\theta = 0°$, 45°, 100 °C, and 155 °C for the same blend cross-linked at 105 °C with *linearly polarized* light (3.0 mW/cm^2).

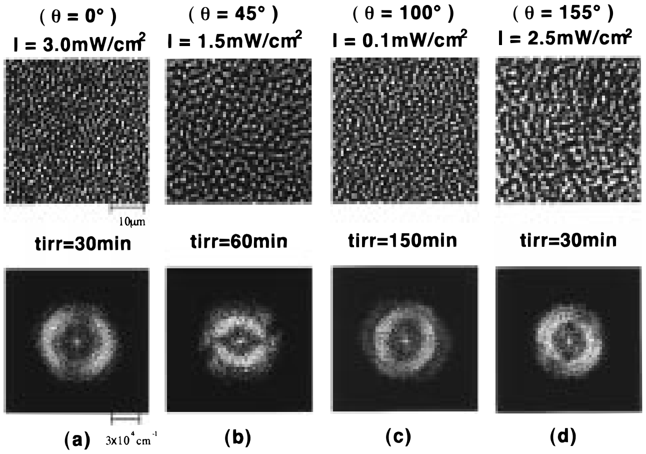

Figure 12. Morphologies and the corresponding 2D-FFT power spectra of PSA/PVME (30/70) blends irradiated at 105 °C by using *unpolarized* light with various intensities. The orientations θ at which the blend receives the equivalent irradiation intensity in the case of linearly polarized light are also indicated in the figure.

would be expressible by a universal law if the effect of the reaction rates is properly compensated.

In Figure 11b, the characteristic length scales ξ obtained for a PSA/PVME (30/70) blend cross-linked with linearly polarized light were plotted versus the reduced reaction time ($t_{\mathrm{irr}} \cos^2 \theta$) in the double-logarithmic scale for the four typical orientations 0°, 45°, 100°, and 155°. The factor ($\cos^2 \theta$) was introduced into the abcissa in order to compensate for the orientational dependence of the reaction rates. It was found that these data did not superimpose on each other because of the dependence of their slopes on the orientation θ. However, shown in Figure 11a are the results obtained for the same PSA/PVME(30/70) blends irradiated by *unpolarized* UV light with the intensities 3.0, 2.4, 1.5 and 0.1 mW/cm^2. These intensities correspond respectively to those received by the blend at the orientation $\theta = 0°$, 155°, 45°, and 100° in the case of irradiation with linearly polarized light. From the reduced plot $\xi(t)$ versus ($t_{\mathrm{irr}} \cos^2 \theta$) in double-logarithmic scale, it was found that all the data almost fall on a straight line, except those obtained with the highest intensity 3.0 mW/cm^2 which corresponds to $\theta = 0°$. The reason for the deviation of the kinetic data observed with this highest intensity is probably due to the contribution of the elastic stress associated with the reaction inhomogeneity which cannot completely relax during the cross-linking reaction. The morphology and the corresponding 2D-FFT power spectra obtained for PSA/PVME(30/70) blends irradiated by *unpolarized* light with different intensities after appropriate irradiation times are shown in Figure 12 for comparison.

The phase-separation kinetics expressed in terms of the reduced plots illustrated in Figures 11a and 11b obtained respectively with unpolarized and polarized light strongly suggests that there exists couplings and/or interference processes among unstable modes propagating with different rates along different orientations in the blend irradiated with linearly polarized light. The morphology observed after an irradiation time is therefore determined by these interactions. Further experiments using *unpolarized* light with adjustable intensity gradients to modify systematically the thermodynamical instabilities of PSA/PVME blends are currently in progress.

IV. Summary and Conclusion

We have demonstrated that linearly polarized light can be used as a tool to select and control the regularity as well as the length scales of the morphology arising from the reaction-induced phase separation. The following results were obtained:

(1) Directional phase separation of binary polymer mixtures can be induced and controlled by using a photo-cross-linking reaction sensitive to linearly polarized light. Under this particular irradiation condition, the cross-linking densities along the direction parallel to the exciting polarization are higher than those in the perpendicular direction. As a result, the concentration fluctuations become orientation-dependent under irradiation.

(2) The anisotropic morphology was generated by two reasons. One is the spatially inhomogeneous distribution of the cross-linking densities generated by the selectivity of photocross-linking reaction. The other is the freezing-in process of polymer diffusion due to the network formation. The latter tends to preserve the broken spatial symmetry of concentration fluctuations under irradiation, giving rise to the formation of lamellar structures.

(3) The anisotropic elastic stress associated with the orientation-dependent cross-link densities of PSA chains in the reacting blend seems to play an important role in the couplings between the local anisotropy of the reaction and the orientation of the morphology in the micrometer scale.

(4) By comparing these data with those obtained by unpolarized light, it was found that the morphology obtained by irradiation with polarized light reflects the interference of various instabilities propagating with different rates at different orientations in the reacting blends.

The experimental results obtained in this work not only suggest a novel method for morphology control of polymer blends using polarized light but also indicate that photo-cross-linked polymer mixtures can provide a physicochemical system to study the selection process of instabilities in polymers.

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