

Reaction-Induced Ordering Phenomena in Binary Polymer Mixtures

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(Received 17 August 1995)

Mesoscopic ordering processes have been found in binary polymer mixtures where only one polymer component was selectively cross-linked by irradiation with ultraviolet light. Depending upon the competitions between the reaction and the phase separation, the mixture can be destabilized and exhibits a wide range of mesoscopic structures such as spatially modulated, concentric (target) and/or labyrinthine patterns in the micrometer range. Our results suggest the existence of a pattern selection process driven by photochemical reactions in polymeric materials.

PACS numbers: 83.80.Es, 82.35.+t, 83.80.Jx

Phase separation kinetics of a mixture quenched from the stable into the unstable regions of the phase diagram has been intensively studied in the past decades for simple liquids, metallic alloys [1], and polymer mixtures [2]. Cahn and Hilliard initially proposed the well-known linearized model to explain the early stage kinetics [3]. As determined by linear stability analysis [4], the spinodal decomposition proceeds exponentially with time in the early stage, with the growth rate determined by the characteristic times of the dominating unstable modes arising under the given condition. In the past decade, the validity of this linearized theory has been experimentally verified for polymer mixtures [5]. However, in practice, the phase separation of polymer mixtures often proceeds under the presence of an external field such as a temperature gradient [6], shear flow [7], or a chemical reaction [8]. It is expected that under these particular conditions the dispersion relation, i.e., the plot of the growth rate versus wave number, of a polymer mixture might be greatly modified, leading to pattern formation processes which are quite different from the conventional spinodal decomposition.

In this Letter, we will experimentally show that the phase separation induced by a photochemical reaction in binary polymer mixtures is a typical example of a pattern selection process where the unstable modes can be regulated and controlled by the reactions. A wide variety of mesoscopic structures can be created by adjusting the competitions between the cross-linking reaction (long-range inhibition) and the phase separation (short-range activation). Furthermore, by changing the reaction rates, we are also able to demonstrate the significant roles of elastic stress associated with the cross-linking.

Polymer blends used in this work are the mixtures of poly(vinyl methyl ether) (PVME, $M_w = 9.6 \times 10^4$, $M_w/M_n = 2.6$), and a styrene-chloromethyl styrene random copolymer [P(S-*stat*-CMS), $M_w = 2.7 \times 10^5$, $M_w/M_n = 1.7$]. These mixtures are known to possess a lower critical solution temperature (LCST), i.e., they undergo phase separation upon heating. The photo-cross-linking reaction was selectively performed by utilizing the photodimerization of anthracenes [9], which are chemically labeled on the P(S-*stat*-CMS)

chains. Details, including chemical synthesis and characterization of these polymers, were described elsewhere [10]. The photo-cross-linking reaction was induced in the one-phase region located between the cloud point curve and the glass transition temperature (T_g) of the blends under three typical conditions, i.e., close to the co-existence curve, in the vicinity of T_g , and in the intermediate region. The average intensity of the Hg-Xe lamp (500 W, Hamamatsu Photonics) used for the cross-linking reaction is $2.5 \text{ mJ/cm}^2 \text{ s}$ at 365 nm. The morphology of the blends after irradiation was observed by using a phase-contrast optical microscope (Nikon, model XF-NTF-21) whose focal plane was adjusted at the center of the sample with thickness $50 \mu\text{m}$. To release the elastic strain accumulated during the reaction, only the middle part ($4 \text{ mm} \times 8 \text{ mm}$) of the sample ($6 \text{ mm} \times 12 \text{ mm} \times 0.05 \text{ mm}$) was irradiated using a metallic mask which allows the elastic strain associated with the reaction to relax toward the uncross-linked peripheral of the sample.

Figure 1 shows the composition dependence of the cloud points and the glass transition temperatures of the P(S-*stat*-CMS)/PVME blend. The temperatures of the cross-linking experiments are also indicated in the same figure. A P(S-*stat*-CMS)/PVME (50/50) blend becomes unstable and undergoes phase separation upon cross-linking at 120°C , which is located at 10.5°C below the cloud point of this particular composition.

The resulting morphology is a spatially modulated structure as revealed by the two-dimensional fast Fourier transform (2D FFT) of the optical micrographs. As an example, the morphology obtained after 40 min of irradiation and its corresponding 2D power spectra are shown in Fig. 2. The characteristic length λ calculated from the 2D power spectra increases with irradiation time and asymptotically approaches a mesoscopic length scale of $2 \mu\text{m}$ after 60 min of irradiation, indicating that the phase separation was arrested by the P(S-*stat*-CMS) networks. The average cross-linking density γ of P(S-*stat*-CMS) chains obtained under this particular condition is 4 junctions/chain as estimated from the decrease in the absorbance of anthracene at 410 nm, which was

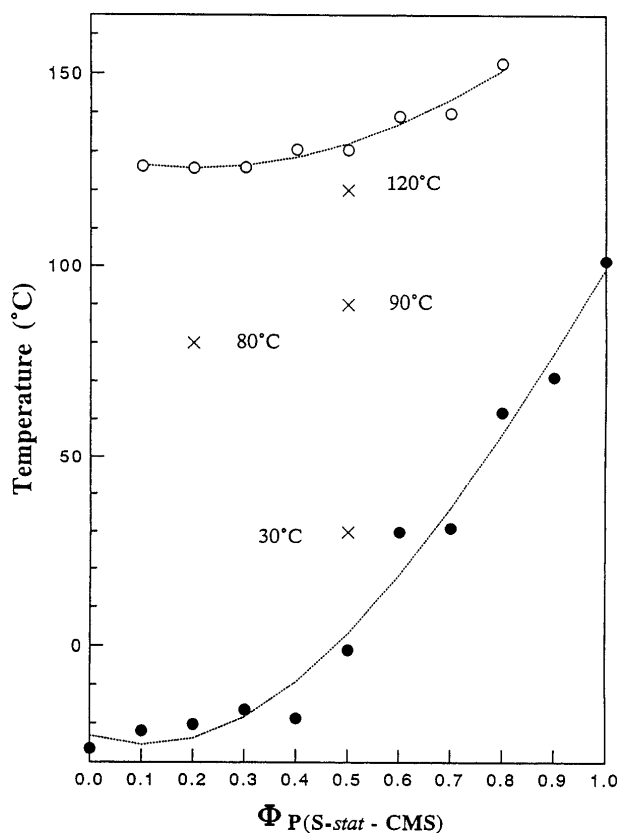


FIG. 1. Composition dependence of the glass transition temperatures and the cloud points of P(S-stat-CMS)/PVME blends. \times indicates the conditions of photo-cross-linking.

monitored until the phase structures become observable by optical microscopy [11].

On the other hand, concentric (target) patterns shown in Fig. 3 emerge when a P(S-stat-CMS)/PVME (50/50)

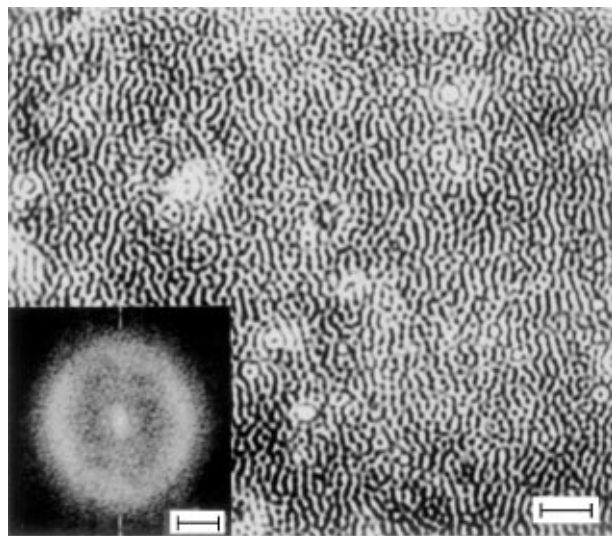


FIG. 2. A phase-contrast optical micrograph and the corresponding 2D FFT power spectra (inset) of a P(S-stat-CMS)/PVME (50/50) blend obtained after irradiation at 120 °C over 40 min. The scales are 10 μm and $2 \times 10^4 \text{ cm}^{-1}$, respectively.

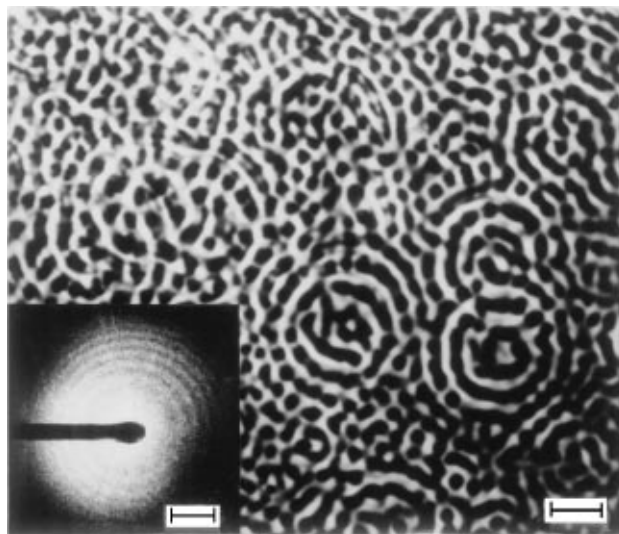


FIG. 3. Morphology and the corresponding light scattering pattern of a P(S-stat-CMS)/PVME (50/50) blend irradiated at 90 °C in 600 min. The scales are 10 μm and $1 \times 10^4 \text{ cm}^{-1}$, respectively.

blend was photo-cross-linked at a lower temperature (90 °C). The blend with these peculiar structures exhibits iridescence under white light. As depicted in the inset of Fig. 3, the diffraction pattern of this sample obtained with a He-Ne laser (632.8 nm) shows higher orders, reflecting the structural regularity of the morphology. These target patterns become observable by optical microscopy after 1 h of irradiation. The dark and bright layers of the morphology correspond, respectively, to the copolymer-rich and PVME-rich phases. At the early stage, the bright and dark layers of these targets are continuous. As irradiation time increases, their contrasts become stronger while their sizes are almost unchanged during the first few hours of the reaction. However, when irradiation time is longer than 6 h, PVME (the bright part) starts appearing and coalesces in the middle of the copolymer-rich region (the dark layers), reducing the thickness of the dark layers to about one-half of its initial scale. Eventually, the layers of these targets become discontinuous and break up into spherical domains with quite regular shape which are mainly responsible for the diffraction patterns with high orders seen in the inset of Fig. 3. The time evolution of this process is illustrated in Fig. 4 where the intensity, measured along a line passing through the center of a target, was plotted against the pixel number. The high and the low brightness correspond, respectively, to the PVME-rich and the P(S-stat-CMS)-rich phases.

The cross-linking density γ corresponding to the morphology shown in Fig. 3 was estimated from UV-visible spectroscopy data as 14 junctions/chain. In these cross-linking experiments, there exists a competition between the reaction, which tends to inhibit the polymer diffusion via the network formation, and the phase separation, which is activated by the reaction. The former

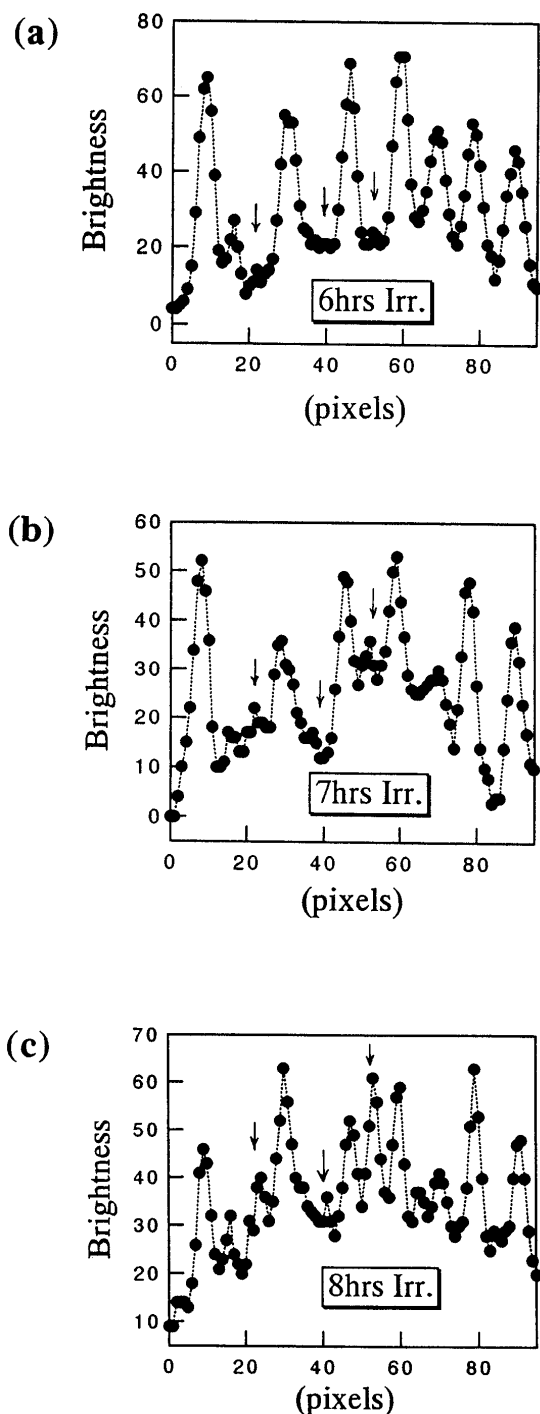


FIG. 4. Time evolution of the target patterns observed after (a) 6 h, (b) 7 h, and (c) 8 h of irradiation. 40 pixels correspond to $10 \mu\text{m}$. The growth of the PVME-rich phases is indicated by the arrows.

effect is dominant for the cross-linking reactions carried out in the vicinity of T_g of the blends, whereas the contribution of the latter is remarkable at temperatures close to the coexistence curve. It is worth noting that when cross-linked at 30°C , i.e., 30.8°C above T_g , the blend undergoes microphase separation with domain sizes limited in the nanometer range upon heating [10].

On the other hand, the glass transition temperature as well as the elastic modulus of the blend increase during the cross-linking reaction. This increment, particularly in elastic modulus, can modify the thermodynamical instability of the blends via the couplings with the concentration fluctuations [12–14]. To elucidate this effect, we performed cross-linking reactions of a P(S-*stat*-CMS)/PVME (20/80) blend at 80°C and compared the data to those obtained with the 50/50 blend. This particular temperature was chosen in order to match the gaps between the experimental temperatures (80 and 90°C) and the cloud points (126 and 139.2°C) of the blends at these two compositions. It was found that when irradiation time increases from 1 to 8 h the morphology of the cross-linked blend undergoes isotropy (spatially modulated structure) \rightarrow anisotropy (lamellalike structure) transition, suggesting the significant contribution of the elasticity of the forming networks to the phase separation process. Furthermore, this structural anisotropy enhances as irradiation time increases. An example of this anisotropic morphology and its corresponding 2D FFT power spectra is shown in Fig. 5 for a P(S-*stat*-CMS)/PVME (20/80) blend photo-cross-linked over 8 h at 80°C . The structures are of lamellalike type with high regularity as revealed by the second-order diffraction in the vertical direction of the 2D power spectra.

As shown in Fig. 6, this isotropy-anisotropy transition can be explained by the cross-linking reaction kinetics monitored for the two compositions (20/80 and 50/50) irradiated at 80 and 90°C , respectively. The slopes of these curves represent approximately the average cross-linking rate. As expected, the cross-linking reaction in the 20/80 blend proceeds faster, and its cross-linking efficiency is higher than the 50/50 blend. The phase separation of the latter begins 15 min after irradiation, preventing the cross-linking reaction from proceeding further.

Because the cross-linking reaction occurs inhomogeneously, there might exist in the irradiated blend several local regions with different cross-linking densities. This speculation is supported by the fact that the cross-linking reaction observed in the one-phase region follows the Kohlrausch-Williams-Watts kinetics [15]. Therefore, it is reasonable to conclude that the structural anisotropy observed in Fig. 5 originates from the elastic modulus gradients induced by this inhomogeneity. The same reason might also be applied to the weak anisotropy appearing in Fig. 2, where the cross-linking reaction was prevented early by the sample cloudiness accompanying the phase separation. Though the mask was used in both cases, the elastic stress associated with the network formation in the 20/80 blend cannot completely relax, because the reaction proceeds faster than the case of the 50/50 blend as revealed in Fig. 6. Consequently, the effects of elastic stress become remarkable as the reaction time increases, resulting in the labyrinthine morphology shown in Fig. 5.

In general, a binary polymer mixture becomes unstable when one component is selectively cross-linked, because

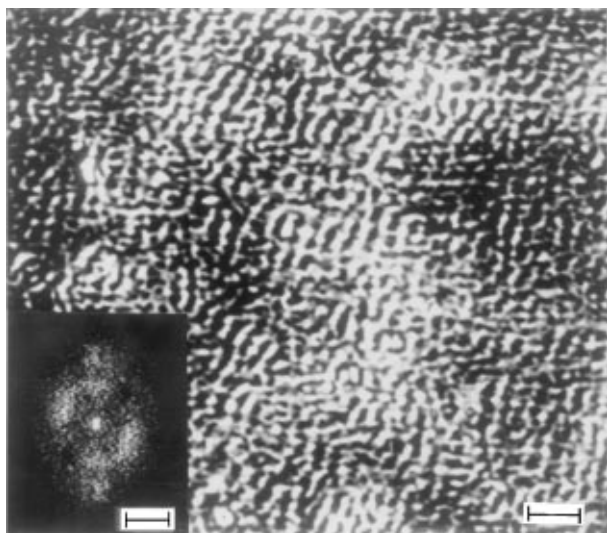


FIG. 5. Morphology and the corresponding 2D FFT power spectra with the second-order diffraction in the vertical direction of a P(S-*stat*-CMS)/PVME (20/80) blend irradiated at 80 °C over 480 min. The scales are 10 μm and $2 \times 10^4 \text{ cm}^{-1}$, respectively.

the network formation gives rise to a decrease in entropy and an increase in elastic free energy of the mixture. The effects of chemical reactions on the spinodal decomposition process have been investigated recently by numerically solving the Cahn-Hilliard equations containing reaction terms which are either linear [16] or nonlinear [17] with respect to concentration. It was found that chemical reactions suppress the growth of unstable modes with long wavelengths in the early stage, and lead to an ordering process at the late stage with labyrinthine and/or hexagonal structures. Experimentally, only the frozen spinodal structures have been observed so far for binary polymer blends, where one polymer component was selectively photo-cross-linked inside the spinodal re-

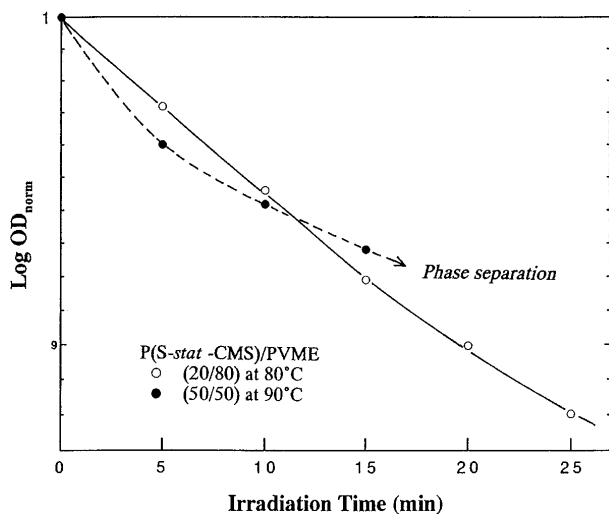


FIG. 6. Photo-cross-linking kinetics monitored at the early stage of irradiation for the 50/50 and 20/80 blends. OD_{norm} is the normalized absorbance of anthracene.

gion [18]. On the other hand, to explain the formation of the target patterns shown in Fig. 3, Furukawa has recently proposed the so-called nucleation-assisted spinodal decomposition mechanism [19]. According to this phenomenological model, the cross-linking reaction first induces nucleation and then pushes the reacted blends into the spinodal region, where the instability takes place around the stable nuclei and forms the target patterns. The computational results, however, do not completely agree with the experimental data. To completely understand the mechanism of pattern formation in reacting polymer blends, we think that a Cahn-Hilliard model for reacting mixtures, with the elasticity effects taken into account, is needed.

We greatly benefited from discussions with R. C. Desai, G. Dewel, H. Furukawa, S. C. Glotzer, K. Sekimoto, and J. Verdasca. The financial support from the Ministry of Education, Science and Culture, Japan (Grant-in-Aid No. 06651052 and No. 07651109), is gratefully acknowledged.

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