Positive feedback driven by concentration fluctuations in asymmetrically photo-cross-linked polymer mixtures

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Spatially coherent structures in the micrometer scales were observed in a binary polymer mixture photo-cross-linked in the miscible region. By following the reaction kinetics, it was found that these structures originated from a positive feedback loop driven by the concentration fluctuations associated with the reaction. The fact that this autocatalytic behavior depends strongly on the reaction kinetics suggests a solution to reconcile the two opposite viewpoints on the role of thermodynamics in formulating the time-dependent Ginzburg-Landau equation for chemically reacting polymer mixtures. [S1063-651X(97)51905-2]

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A large number of coherent spatiotemporal structures have been found in systems containing feedback loops driven by an external control parameter [1,2]. In physical systems, one such structure is the hexagonal or the roll pattern emerging from the Rayleigh-Bénard instability. The control parameter in this case is the temperature gradient which drives the feedback loop composed of the buoyancy of the liquid and its heat dissipation [3]. On the other hand, in most chemical systems, the feedback processes arise from the autocatalytic intermediate steps of chemical reactions such as the Belousov-Zhabotinsky (BZ) reaction [4]. From the viewpoint of materials science, a wide variety of ordered structures can be designed if some feedback loops adjustable by external fields are incorporated into the materials.

Recently, in an effort to develop an efficient method to control the morphology of polymer mixtures, we have utilized photo-cross-linking reactions to regulate the instabilities arising from chemically reacting mixtures [5–7]. In these experiments, the cross-linking reactions were carried out by taking advantage of the photodimerization of anthracenes which are chemically labeled on poly(styrene-*co*-chloromethylstyrene) (PSCS). By this reaction, only the PSCS chains form the networks in the mixtures with poly(vinyl methyl ether) (PVME) upon irradiation with ultraviolet light. As shown in Fig. 1(a), a PSCS-PVME (20-80) mixture photo-cross-linked at 80 °C becomes unstable and exhibits lamellar domains having the same orientation extending over almost 100 μm. This spatial coherence increases with increasing the reaction rates by irradiation with light of higher intensity as illustrated in Fig. 1(b). There are several possible mechanisms for the formation of these structures. The asymmetric interactions of the two polymer components of the blends with the glass substrate, i.e., the wetting effect [8], might be one of the reasons responsible for these peculiar patterns. However, it is well known that for polystyrene–poly(vinyl methyl ether) (PS-PVME) blends, this effect is only remarkable for the samples with thickness

less than 10 μm [9]. This critical length scale is much smaller than the thickness 50 μm of the samples used in this work. On the other hand, it has been known that coherent structures can also arise from the convection induced by chemical reactions [10–12]. For polymers, particularly in the bulk state, the photo-cross-linking reactions cannot induce convection because of the extremely high viscosity of the mixtures which gradually increases as the reaction proceeds.

In this paper, we show that one of the mechanisms responsible for the emergence of these spatially coherent structures is the positive feedback loop driven by the reaction-induced concentration fluctuations in the cross-linked mixtures.

All the characteristics of the polymers used in this work as well as the experimental procedure were reported in detail elsewhere [5–7]. Since the PSCS-PVME blend possesses a lower critical solution temperature (LCST), the new coexistence curve of the reacting blends shifts toward the side of lower temperatures upon cross-linking. In general, there exist two limiting cases for the photo-cross-linking reactions. One is performing the reaction at temperatures close to the coexistence curve of the unreacted blends and the other is in the vicinity of their glass transition temperatures (T_g). These two cases correspond respectively to the ''deep'' and ''shallow'' quench conditions because the cross-linking density is low in the former and is high in the latter cases. Under the shallow quench conditions, the coexistence curve of the reacting blends does not reach the experimental temperature (T_{expt}) because of the high cross-linking densities. For these particular cases, the cross-linking reaction does not follow the mean-field kinetics and can be well expressed by the modified Kohlrausch-Williams-Watts (KWW) or the stretched exponential function [13]:

$$\mathcal{D}(t) = (\mathcal{D}_0 - B)\exp[-(k_0 t)^\beta] + B, \tag{1}$$

Here, $\mathcal{D}_0$ and $\mathcal{D}(t)$ are the optical densities of the cross-linker at the irradiation time $t=0$ and t. The constant B is introduced into the KWW equation in order to compensate for the presence of unreacted anthracenes in the mixture after irradiation over a long time. k_0 and β are the average cross-linking rate and the exponent describing the inhomogeneity of the reaction. An example is shown in Fig. 2 for a

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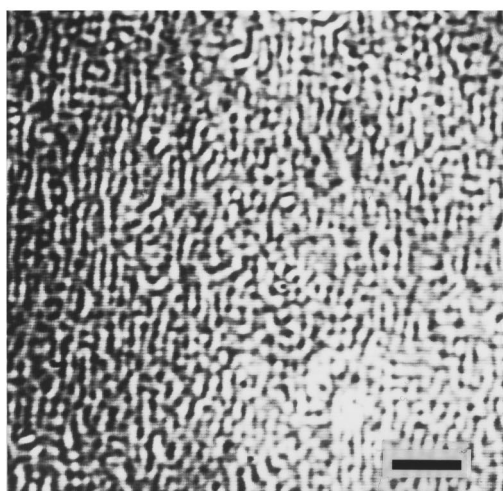
(a)
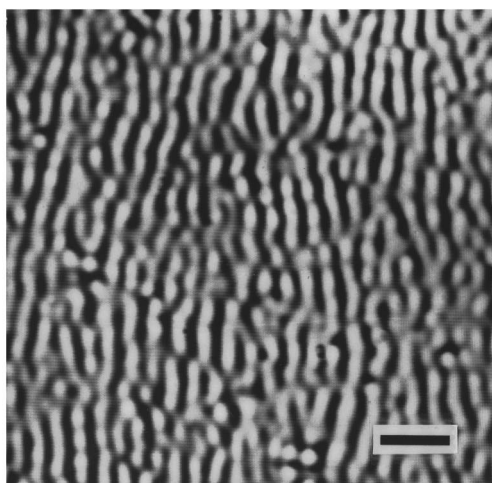
(b)

FIG. 1. Spatially coherent structures obtained by photo-cross-linking PSCS-PVME mixtures: (a) a (20-80) blend at 80 °C; (b) a (50-50) blend at 90 °C. The scale is 10 μm. The reaction times are 240 and 600 min for (a) and (b), respectively. The reaction rate for case (b) is about threefold larger than case (a).

PSCS-PVME (50-50) blend photo-cross-linked at different temperatures under the shallow quench conditions. The gaps between the T_{expt} and the cloud point are 106.2, 91.2, and 76.2 °C. β is in the range 0.6–0.7 and slightly increases with increasing temperature, implying that the cross-linking reaction proceeds inhomogeneously in the blend. The validity of the KWW relaxation mechanism for these cases can be explained by the fact that the reaction is relatively fast at the early stage and is slowed down at later times because of the increase in viscosity associated with the network formation and the decrease in the concentrations of anthracene. On the other hand, the mixture undergoes phase separation when the cross-linking density exceeds a critical value under the deep quench conditions. The peculiar behavior of the reaction was observed when the cross-linking was carried out at tempera-
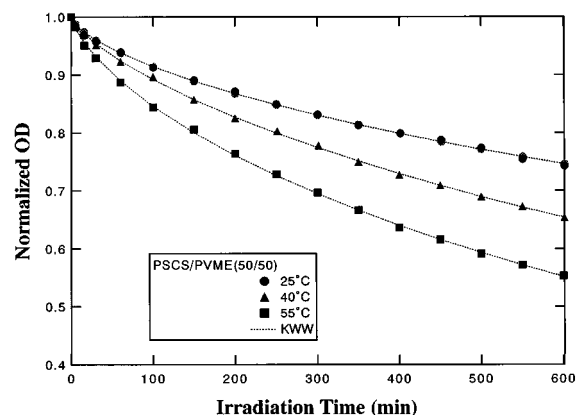

FIG. 2. Reaction kinetics of a PSCS-PVME (50-50) blend photo-cross-linked at different temperatures under the shallow quench conditions. The dotted curve was obtained by fitting the experimental data to Eq. (1).

tures close to the coexistence curve. As shown in Fig. 3 as an example, the absorbance of anthracene measured at 410 nm normalized by its initial value is plotted versus irradiation time for a PSCS-PVME (20-80) blend photo-cross-linked at 80 °C which is located at 45.8 °C below the phase boundary of the unreacted mixture. The concentration of anthracene decreases quickly within 5 min of irradiation, then exhibits an inflection point and decays again before phase separation takes place. The onset of the phase separation was detected by the abrupt increase indicated by the arrow in the absorbance of the irradiated mixture monitored simultaneously at 500 nm, outside the absorption range of the two polymers as well as of anthracene. To examine the reaction kinetics, the average reaction rate $\langle k \rangle = dp/dt$ was calculated from the decay of the normalized absorbance of anthracene. Here t is the irradiation time and p is the reaction yield defined as

$$p(t) = \frac{\mathcal{D}_0 - \mathcal{D}(t)}{\mathcal{D}_0} \qquad (2)$$

where $\mathcal{D}_0$ and $\mathcal{D}(t)$ are the absorbances of the photo-cross-linker measured at irradiation time 0 and t.
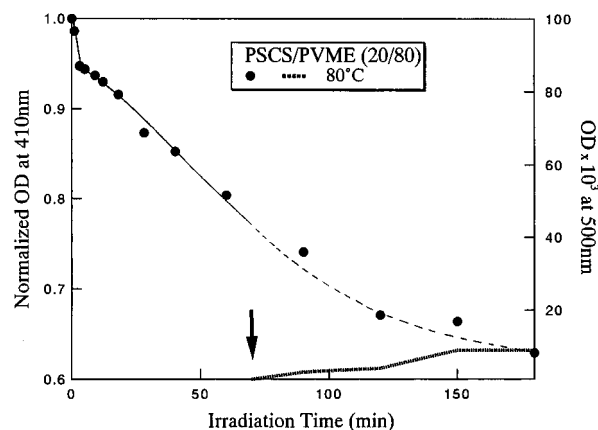

FIG. 3. Cross-linking kinetics of a PSCS-PVME (20-80) obtained at 80 °C, under a deep quench condition. Phase separation induced by the cross-linked reaction becomes observable at 60 min after irradiation as indicated by the arrow.
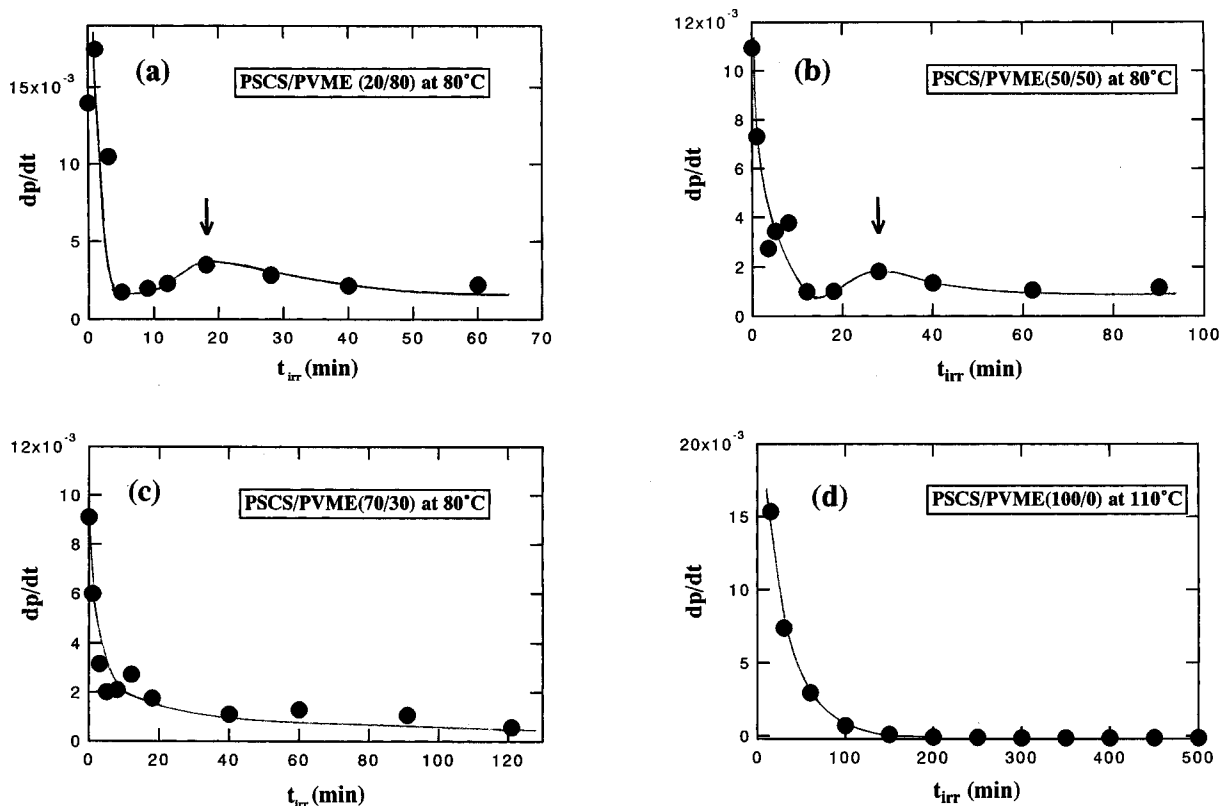
FIG. 4. Dependence of the average reaction rate $\langle k \rangle$ on irradiation time: (a) PSCS-PVME (20-80), (b) (50-50), and (c) (70-30) at 80 °C; (d) homopolymer PSCS at 110 °C.

The variation on the average reaction rate $\langle k \rangle$ with irradiation time t is shown in Fig. 4 for the three compositions PSCS-PVME (20-80), (50-50), and (70-30) cross-linked at 80 °C located at 45.8, 50.5, and 72.7 °C from the phase boundary of the mixture. As depicted in Fig. 4(a), the average reaction rate $\langle k \rangle$ obtained for a PSCS-PVME (20-80) blend first decreases with increasing irradiation time within 5 min of irradiation, then passes through a maximum at 20 min and eventually decreases again before the phase separation takes place after 60 min of irradiation. The similar behavior of $\langle k \rangle$, though somewhat weaker, was also observed with a PSCS-PVME (50-50) cross-linked at the same temperature. On the other hand, $\langle k \rangle$ decays almost monotonously with irradiation time for a PSCS-PVME (70-30) blend as shown in Fig. 4(c). The maximum of the plot (dp/dt) vs t_{irr} where t_{irr} is the irradiation time, shifts toward the longer time as the composition of the high T_g component (PSCS) increases. Furthermore, this self-accelerating behavior becomes insignificant with decreasing the ''quenching depth,'' i.e., carrying out the reaction at lower temperatures far from the cloud points. From these results, it can be concluded that the cross-linking reaction of PSA-PVME blends exhibits autocatalytic behavior under the ''deep quench'' conditions. This autocatalysis is most significant for PSCS-PVME (20-80) blends cross-linked at 80 °C whereas it is not remarkable for a PSCS-PVME (70-30) blend cross-linked at the same temperature as seen in Fig. 4. The origin of this autocatalysis is revealed by comparing these experimental results with the average reaction rate $\langle k \rangle$ obtained for a PSCS *homopolymer* cross-linked at 110 °C, i.e., 10 °C above its glass transition temperature as shown in Fig. 4(d). Obviously, $\langle k \rangle = dp/dt$

decreases monotonously with irradiation time and did not exhibit the autocatalytic behavior as observed for polymer mixtures. Therefore, it can be concluded that the autocatalytic feedback shown in Fig. 4 originates from the concentration fluctuations induced by the photo-cross-linking reactions at the experimental temperature (T_{expt}). Namely, PSCS-PVME blends become unstable upon cross-linking. As the coexistence curve approaches the T_{expt}, both the amplitudes and the wavelengths of the concentration fluctuations increase. Under this circumstance, the PSCS-rich and the PVME-rich domains start forming temporarily in the mixture. Though the average number of anthracenes decreases during the reaction, depending upon the experimental conditions, their average distances in the PSCS-rich domains might increase due to the condensation effect induced by these concentration fluctuations. As a result, the reaction is accelerated and shifts the phase boundary closer to the experimental temperature. This process, in turn, amplifies the fluctuations in the reacted blends, forming a positive feedback loop between the cross-linking reaction and the fluctuations. It should be noted that the autocatalysis of the cross-linking reaction described above is completely different from those arising from chemical reactions involving radical formation processes through which heat is generated during the reactions such as radical polymerization [14] and curing reactions of epoxy resin [15]. In contrast with these mechanisms, the autocatalysis observed in this work has a thermodynamic origin and is driven by concentration fluctuations.

The experimental results described above provide a most probable explanation for the spatially coherent structures illustrated in Fig. 1. Namely, the inhomogeneity of the cross-
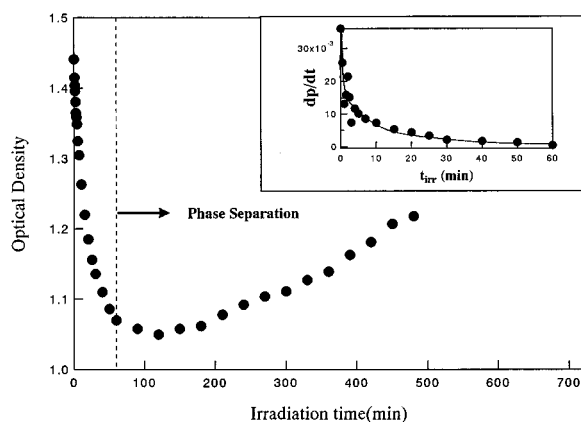
FIG. 5. *Trans→cis* photoisomerization of stilbene chemically labeled on PSCS chains in a PSCS-PVME (20-80) blend observed at 90 °C. The exciting and monitoring wavelengths are 365 and 355 nm, respectively. The mixture undergoes phase separation at 60 min after irradiation. Inset: irradiation time dependence of the reaction rate $\langle k \rangle$.

linking reactions is amplified by the autocatalytic feedback induced by the concentration fluctuations in the reacting blends. As a result, the gradients of the elastic modulus arising from the network formation are strongly magnified during the reaction, resulting in lamellar structures in the micrometer scale. This positive feedback loop depends strongly on the cross-linking rates. In other words, the light intensity and the label content of the cross-linker anthracene determine the extent of coherence of the morphology. It should be noted that for the reversible *trans⇔cis* photoisomerization of the stilbene molecules chemically attached to PSCS chains, the autocatalytic behavior was not observed in the same PSCS-PVME (20-80) blend irradiated at 90 °C, i.e., 17 °C below the coexistence curve of the unreacted blend, as shown in Fig. 5. In contrast to the case of photo-cross-linking of anthracene where the long-range diffusive motions are required for the intermolecular reaction, only intramolecular rotations around the double bond are necessary for the *trans⇔cis* photoisomerization of stilbene to occur. The average reaction rate $\langle k \rangle$ of this unimolecular reaction exhibits a monotonous decrease with increasing irradiation time, resembling the behavior shown in Fig. 4(d) for the homopolymer PSCS. In this particular case, the mixture is thermodynamically destabilized by the increase in polymer segmental volumes accompanying the *trans→cis* transformation of stilbene. Therefore, it can be concluded that the environmental influence is significant in bimolecular diffusion-controlled reactions such as the photodimerization of anthracene shown above and elsewhere [16], but it is not remarkable for the case of unimolecular reactions such as the photoisomerization of stilbene. The results described here could provide, from the experimental side, a solution to reconcile the two opposite viewpoints on the contributions of thermodynamics to the chemical reactions in the time-dependent Ginzburg-Landau equation for chemically reacting mixtures [17,18]:

$$\frac{\partial \phi(r,t)}{\partial t} = M\nabla^2 \frac{\delta F\{\phi(r,t)\}}{\delta\phi(r,t)} + g(\phi) \qquad (3)$$

where $\phi(r,t)$, M, and $F\{\phi(r,t)\}$ are respectively the order parameter, the mobility, and the free energy functional of the mixture. The contribution of the chemical potential of the mixture to the reaction rate k contained in the reaction term $g(\phi)$ of Eq. (3) might be greatly significant for bimolecular reactions whereas it is much less pronounced for unimolecular reactions.

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