

## Soft-mode suppression in the phase separation of binary polymer mixtures driven by a reversible chemical reaction

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Soft-mode suppression driven by a reversible photoisomerization was experimentally observed in the phase separation process of polystyrene derivatives–poly(vinyl methyl ether) (PS-PVME) mixtures. The phase separation was controlled by manipulating, with ultraviolet light, the reversible changes in polymer segmental volumes associated with the *trans-cis* conformational transitions of *stilbene* molecules chemically attached on the PS chains. It was found that when the rate of the forward *trans*→*cis* reaction is comparable to its backward *cis*→*trans* process, the phase separation becomes extremely slow and follows the Lifshitz-Slyosov-Wagner law  $t^\alpha$  with  $\alpha$  less than 0.1, whereas  $\alpha$  is in between  $\frac{1}{4}$  and  $\frac{1}{3}$  when the reaction is turned off. [S1063-651X(97)51807-1]

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Phase separation that is induced by reversible chemical reactions in a binary mixture is an interesting and important phenomenon which is related not only to practical problems such as morphology control in materials science, but also to many fundamental aspects of spatio-temporal behavior of systems with competing interactions [1]. The characteristic length scales of these systems are, in principle, determined by the competitions between the two antagonistic interactions: the reversible reaction acting as a long-range inhibition and the phase separation playing the role of a short-range activation process. Depending upon the balance of these two interactions, a wide range of ordered structures known as modulated phases [2] has been observed in photo-cross-linked polymer mixtures [3]. For phase separation that is associated with reversible chemical reactions, it has been shown by linear stability analysis that the soft modes, i.e., the unstable modes with long wavelengths, are suppressed by the chemical reactions [1,4,5]. As a consequence, the phase separation might be frozen. These conclusions were derived from the linear stability analysis of the modified time-dependent Ginzburg-Landau equation

$$\frac{\partial \phi(r,t)}{\partial t} = M \nabla^2 \frac{\delta F\{\phi(r,t)\}}{\delta \phi(r,t)} + g(\phi), \quad (1)$$

where  $\phi(r,t)$ ,  $M$ , and  $F\{\phi(r,t)\}$  are, respectively, the order parameter, the mutual mobility, and the free energy functional of the mixture.

The additional term  $g(\phi)$  containing the corresponding reaction kinetics was introduced into Eq. (1) in order to express the contribution of the chemical reactions. So far, Eq. (1) with the first order [4] and more complex [1,5] reactions have been examined and the suppression of the long-wavelength modes has been found by both linear stability analysis and numerical simulation. However, from the general viewpoint of thermodynamics, there have been some questions about the validity of Eq. (1) and the suppression of

the soft modes as well, because the reaction term  $g(\phi)$ , in principle, is governed by the free energy of the mixture [6]. Although the soft mode suppression by chemical reactions is an important problem not only for materials science, but also for fundamental studies on the mode-selection processes in systems out of equilibrium, to the best of our knowledge, no experiments have done so far to verify this important prediction.

In this paper, we will experimentally show that the phase separation process of polystyrene derivatives–poly(vinyl methyl ether) (PS-PVME) mixtures is considerably suppressed by the reversible photoisomerization of the stilbene moieties chemically labeled only on the PS chains. It is well known that upon irradiation with ultraviolet (uv) light of long wavelengths, the *trans*-stilbene isomer undergoes intramolecular rotation around the double bond C=C and transforms into the *cis*-isomer, as schematically shown in the inset of Fig. 1 [7]. The reverse process, on the other hand, can be performed by using uv light of shorter wavelengths. Because the *trans*-

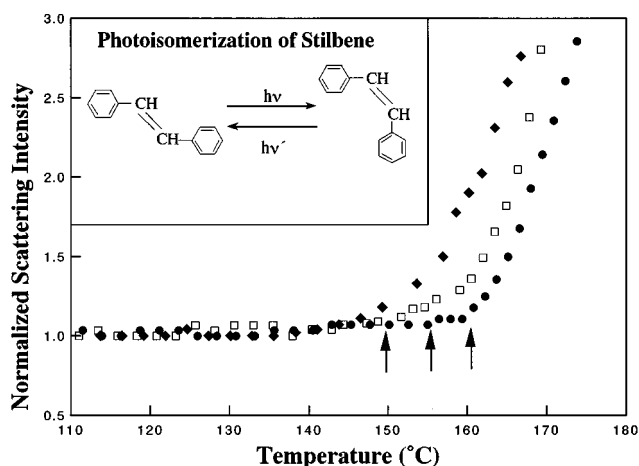


FIG. 1. Destabilization of a *t*-PS–PVME (20-80) blend upon irradiation with 365-nm uv light at 30 °C over different time intervals: (●), 0 min; (□), 120 min; (◆), 360 min. The arrows indicate the temperatures at which the critical scattering becomes observable.

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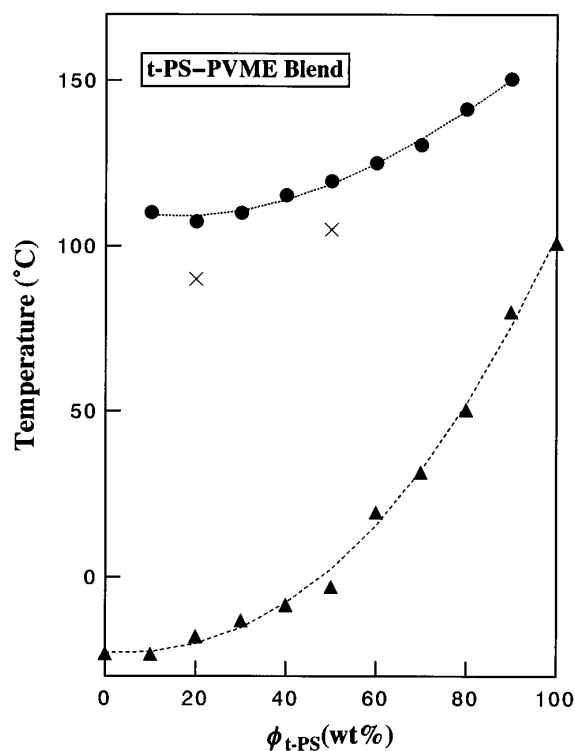
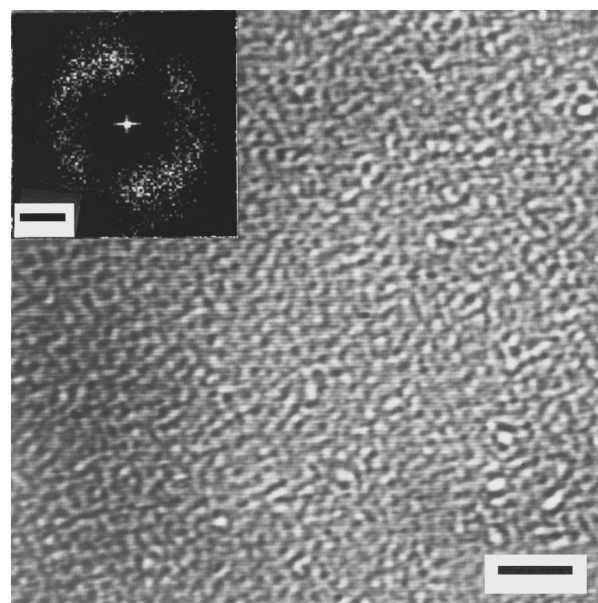
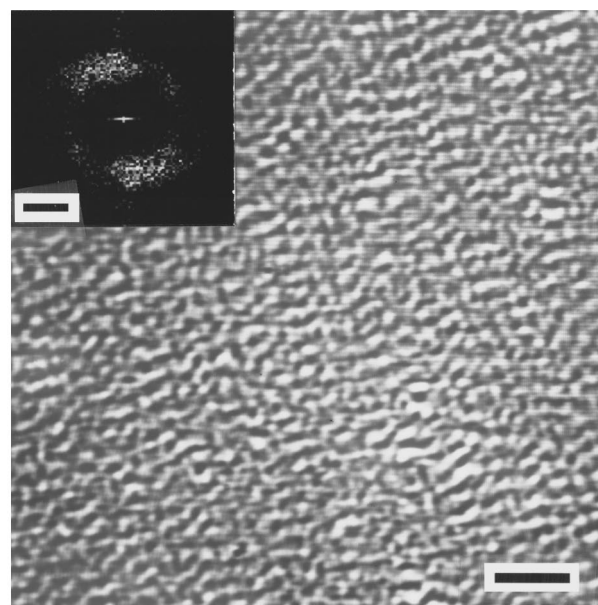


FIG. 2. Upper curve: the cloud point curve of the *t*-PS-PVME blend measured by light scattering after extrapolation to the zero-heating rate. Lower curve: the glass transition temperature obtained by DSC with the heating rate 5 °C/min. (X) indicates the experimental temperatures.

isomer has the planar conformation and is much less bulky than the *cis*-isomer, the *trans*→*cis* transformation destabilizes the mixtures by increasing the polymer segmental volumes, whereas the *cis*→*trans* change has the opposite effects. Since the mixtures of *trans*-PS and *cis*-PS prepared by irradiation of the *trans*-PS with uv light are miscible, the phase separation observed by irradiating a *trans*-PS-PVME blend is probably due to the unfavorable interactions between the *cis*-PS and PVME. A preliminary result has been previously demonstrated for the effect of photoisomerization on the miscibility of a PS-PVME blend [8]. The characteristics of the polymers used in this work have been reported previously [3], except the stilbene-labeled polystyrene derivatives, which were synthesized by coupling the potassium salt of 4-hydroxy stilbene to the polystyrene slightly chloromethylated via copolymerization with chloromethyl styrene [9]. The average label content of the PS chains is one stilbene per 20 repeating monomer units. Irradiation was performed with a high-pressure mercury-xenon lamp (250 W, Moritex, Japan). The finite bands of wavelengths around the two lines 313 and 365 nm from the light source were selected by using appropriate optical filters. The morphology of the blends after irradiation over different time intervals was observed by using a phase-contrast optical microscope (Nikon, model no. XF-NTF-21). The focal plane was adjusted at the center of the sample with the thickness 50  $\mu\text{m}$ . The optical micrographs were digitized and subsequently transferred to a digital image analyzer (Pias, LA-525, Japan) for further analysis. The characteristic length scales of the morphology were calculated from the Bragg conditions  $\xi$



(a)



(b)

FIG. 3. (a) A phase-contrast optical micrograph and the corresponding 2D-FFT power spectra (inset) of a *t*-PS-PVME (20-80) blend observed at 120 min after irradiation with 313-nm uv light at 90 °C; (b) the same blend observed at 240 min. The scales for the image and the power spectra are 10  $\mu\text{m}$  and  $2 \times 10^4 \text{ cm}^{-1}$ , respectively.

$=2\pi/q_{\text{max}}$ , where  $q_{\text{max}}$  was obtained by the circular or sector averages of the two-dimensional power spectra given by the fast Fourier transform (2D-FFT) of the isotropic and anisotropic morphologies.

Shown in Fig. 2 are the glass transition temperatures ( $T_g$ ) and the cloud points of *trans*-stilbene labeled

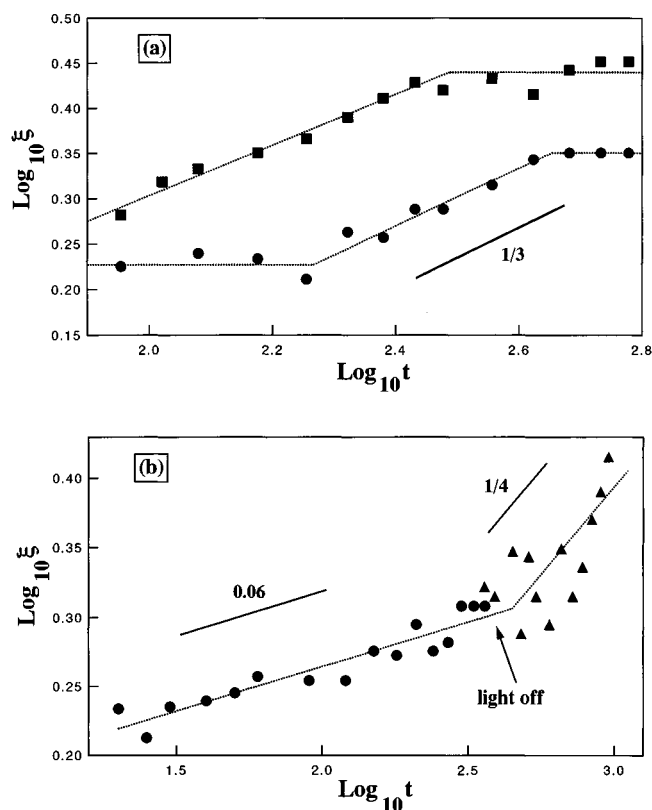


FIG. 4. Coarsening processes of (a) a *t*-PS–PVME (20-80) blend irradiated with uv light at 313 nm with different intensities ( $I_r$ ) at 90 °C; upper line,  $I_r=4.1$  mW; lower line,  $I_r=1.6$  mW; (b) a *t*-PS–PVME (50-50) blend irradiated with uv light at 365 nm (3 mW). The light was turned off at 360 min.

polystyrene–poly(vinyl methyl ether) (*t*-PS–PVME) blends measured respectively by differential scanning calorimetry (DSC) and light scattering at a fixed angle (20°). Upon irradiation with uv light at 365 nm, the temperature at which a *t*-PS–PVME (20-80) blend labeled with one stilbene per 40 repeating monomer units exhibits critical scattering, gradually shifts toward the side of lower temperatures as irradiation time increases. This fact indicates that the two-phase region of the blend has increased due to the *trans*→*cis* transformation of the stilbene molecules labeled on the PS chains. As a result, a *t*-PS–PVME blend initially set at a temperature close to its phase boundary in the one-phase region will undergo phase separation upon irradiation with uv light. The fraction of the *trans*- and *cis*-isomers generated in the blend is determined by the ratio  $\rho$  between their molecular extinction coefficients  $\epsilon$  at the excitation wavelength. The ratio  $\rho = \epsilon_{trans}/\epsilon_{cis}$  at 313 nm is ca. 4.3 as estimated from the absorption data of 4-methoxy stilbene [10], the model compound of the stilbene moieties labeled on the PS chains. On the other hand, the difference in the molecular extinction coefficients of these two isomers at 365 nm is not significant because this particular wavelength is close to the absorption edge of the molecule. Therefore, the *trans*→*cis* transformation is dominating upon irradiating the blend with 313-nm light, whereas it is less significant in comparison with the reverse *cis*→*trans* process when irradiating with uv light at 365 nm.

Upon irradiation using light at 313 nm with the intensity

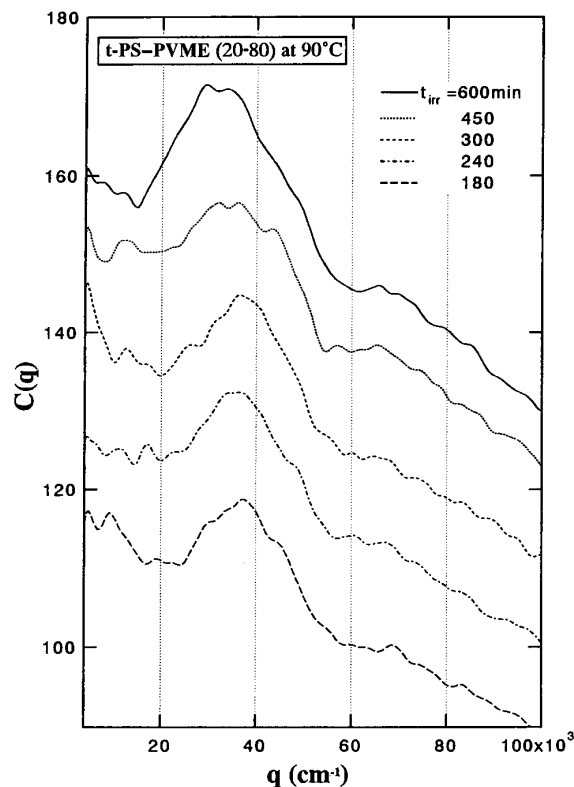


FIG. 5. Time evolution of the 1D power spectra of a *t*-PS–PVME (20-80) blend irradiated with 365-nm uv light (3 mW) at 90 °C.  $t_{irr}$  is the irradiation time. The ordinate is expressed in arb. units.

4.1 mW/cm<sup>2</sup>, phase separation of a *t*-PS–PVME blend (20-80) becomes observable under a phase-contrast optical microscope at 60 min after irradiation. In the early time, the morphology is an isotropic modulated structure as shown in Fig. 3(a) for a blend obtained after 120 min of irradiation. The characteristic lengths  $\xi$  of the structures calculated from the corresponding 2D power spectra increase with increasing irradiation time. Subsequently, the morphology turns from isotropic modulated structures to anisotropic lamellae as illustrated, as an example, in Fig. 3(b) for the same blend obtained at 240 min after irradiation. The coarsening process at this stage follows the Lifshitz-Slyosov-Wagner (LSW) law [11,12]  $\xi(t) \propto t^\alpha$  with  $\alpha=0.29$ . Eventually, the phase separation is frozen at 250 min after irradiation probably due to the increase in the glass transition temperature of the PS-rich domains. Similar behavior of phase separation has been observed previously with photo-cross-linked blends [3,9] and gelation associated with phase separation [13]. Under this irradiation condition, the phase separation was not suppressed by the reaction because the *trans*→*cis* process is dominating. On the other hand, by irradiation with uv light of the same wavelength (313 nm) but with the lower intensity 1.6 mW/cm<sup>2</sup>, the phase separation kinetics of the same blend exhibits three distinct regions within 600 min of irradiation. For the first 200 min of the reaction, the characteristic length scales  $\xi$  were almost unchanged with the reaction time, suggesting that the reacting mixture might pass through the linear region predicted by the Cahn-Hilliard theory [14]. Subsequently, these structures grow and turn from isotropic modulated structures to anisotropic lamellae. This morpho-

logical transition process is similar to that obtained with uv light of higher intensity. The coarsening in the middle stage between 200 to 500 min can be expressed by the LSW relation with  $\alpha=0.31$ . Eventually, the phase separation under this reaction condition is frozen at 500 min after irradiation. These kinetics were summarized in Fig. 4. The fact that, upon irradiation with strong uv light ( $4.1 \text{ mW/cm}^2$ ), the initial region with a constant  $\xi$  was not observed and the pinning process takes place early around 200 min after irradiation, is probably due to the increase in the rate of the *trans*→*cis* transformation, which accelerates the phase separation process. On the other hand, the phase separation process of a *t*-PS–PVME blend with the *same* composition (20-80) irradiated with 365-nm uv light at the *same* temperature ( $90 \text{ }^\circ\text{C}$ ) proceeds extremely slow. As far as observed by phase-contrast optical microscopy, the phase separation of this mixture starts at 150 min after irradiation. As shown in Fig. 5, the maxima of the 1D power spectra obtained from the 2D-FFT of the corresponding optical micrographs were almost unchanged over 300 min of irradiation and only shifts very slightly to the side of low frequency at later time. During the first 300 min of irradiation, the position of the broad peaks around  $3.7 \times 10^4 \text{ cm}^{-1}$  is unchanged, while the morphological transformation from isotropic modulated to lamella structures starts at 210 min after irradiation. It should be noted that the lamella structures observed here do not have any preferential directions. This self-ordering phenomenon has been mentioned previously in numerical calculations for systems undergoing phase separation with long-range interactions [5,15]. From the experimental results obtained under the three different conditions described

above, it can be concluded that, though *not completely frozen*, the phase separation of the *t*-PS–PVME (20-80) blend was strongly suppressed by the reversible *trans*↔*cis* photoisomerization of stilbene induced by irradiation with 365-nm uv light. Finally, as depicted in Fig. 4(b), the evidence of this suppression becomes more obvious with a *t*-PS–PVME 50-50 blend irradiated with 365-nm light at  $105 \text{ }^\circ\text{C}$ , which is located at  $5 \text{ }^\circ\text{C}$  above  $T_g$  of the PS. The coarsening process is very slow and expressible by the LSW-like law with  $\alpha \sim 0.06$  under irradiation with uv light at 365 nm, whereas it is considerably accelerated in the dark (in the absence of the photoisomerization) with  $\alpha$  in between  $\frac{1}{4}$  and  $\frac{1}{3}$ .

In conclusion, the results described in this work provide the experimental evidence of the soft-mode suppression in the phase separation driven by a reversible chemical reaction. Because these unstable modes can be actually tuned and controlled by the reaction, the above results reveal a possibility for studying the mode-selection processes in polymers by taking advantage of chemical reactions.

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