Communications to the Editor

Experimental Verification of a Scaling Law for Phase Separation Kinetics of Reacting Polymer Mixtures

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Received October 31, 1995

Phase separation of polymer mixtures in the presence of chemical reactions has been of great interest, both practically and academically. From the practical aspects, this is strongly related to the reactive melt blending techniques which have been widely utilized in polymer processing to control the morphology of multiphase materials.[1] Fundamentally, the phase separation accompanied by chemical reactions is a typical wavelength-selection process dictated by the competitions between antagonistic interactions at different length scales.[2] Recently, it has been recognized that phase separation in reacting polymer systems has the capability of exhibiting a wide range of ordered structures due to the interplay of the short-range activation (phase separation) and long-range inhibition (chemical reaction).[3] By using stability analysis, Glotzer and coworkers have shown that the instabilities with long wavelengths (the soft modes) in a reacting mixture can be suppressed by chemical reactions, consequently giving rise to the pinning of the spinodal decomposition. These authors also proposed a scaling function for the time evolution of the morphology in this particular case.[4] According to these results, the characteristic length scale $\xi(t)$ of the structures follows the scaling law

$$\xi(t) = t^{\alpha}G(x) \qquad (1)$$

where

$$x = kt$$

Here k and t are the reaction rate and the reaction time, respectively. α is an exponent characterizing the growth of these structures before the pinning process takes place.

In the past few years, we have utilized photochemical reactions to control the phase separation kinetics of binary polymer blends.[5] According to these results, the spatially modulated structures developing during the spinodal decomposition process were efficiently frozen when the blends were cross-linked inside the unstable region under appropriate conditions.[6] Recently, we have also examined the effects of photo-cross-linking reactions on the stability of miscible polymer mixtures.[7] It was found, in this particular case, that the phase separation was induced and eventually arrested by the reaction. In this communication, the validity of the scaling law given in eq 1 was examined by using these experimental data.

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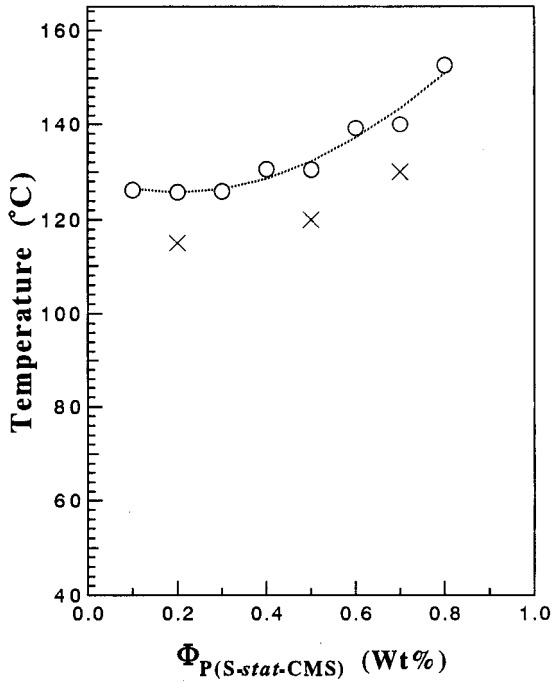

Figure 1. Experimental conditions for the photo-cross-linking reactions: (○) clouding points obtained by light scattering after extrapolating to zero-heating rate; (×) experimental temperatures.

Polymer blends used in this work are mixtures of poly(styrene-*stat*-(chloromethyl)styrene) [P(S-*stat*-CMS)] ($M_w = 2.6 \times 10^5$, $M_w/M_n = 1.5$) and poly(vinyl methyl ether) (PVME, $M_w = 9.6 \times 10^4$, $M_w/M_n = 1.8$). The preparation as well as characterization of these samples are already reported elsewhere.[7] The photo-cross-linking reactions were carried out in the miscible region of the three compositions P(S-*stat*-CMS)/PVME (20/80), (50/50), and (70/30) at 110, 120, and 130 °C, respectively, as schematically indicated in Figure 1. The distances between these experimental temperatures and the cloud points of these three compositions are 15, 10, and 10 °C, respectively. Upon irradiation with ultraviolet light at 365 nm, anthracene moieties chemically labeled on the P(S-*stat*-CMS) chains undergo photodimerization and form P(S-*stat*-CMS) networks in the blend. Under this circumstance, these blends become thermodynamically unstable and undergo phase separation via the spinodal decomposition process because the two-phase region of the blend reaches the experimental temperature. The evolution of the morphology was followed over different time intervals by using phase-contrast optical microscopy. For example, the morphology of a P(S-*stat*-CMS)/PVME (20/80) blend obtained after cross-linking at 110 °C in 25 min is shown in Figure 2a. The corresponding power spectra obtained from two-dimensional fast Fourier transform (2D-FFT) are illustrated in Figure 2b, revealing the bicontinuity of the morphology. Similar results were also observed for P(S-*stat*-CMS)/PVME (50/50) and (70/30) blends. The evolution of these structures was analyzed from the irradiation time dependence of the Bragg spacing $\xi = 2\pi/q_{max}$ where

S0024-9297(95)01627-5 CCC: $12.00

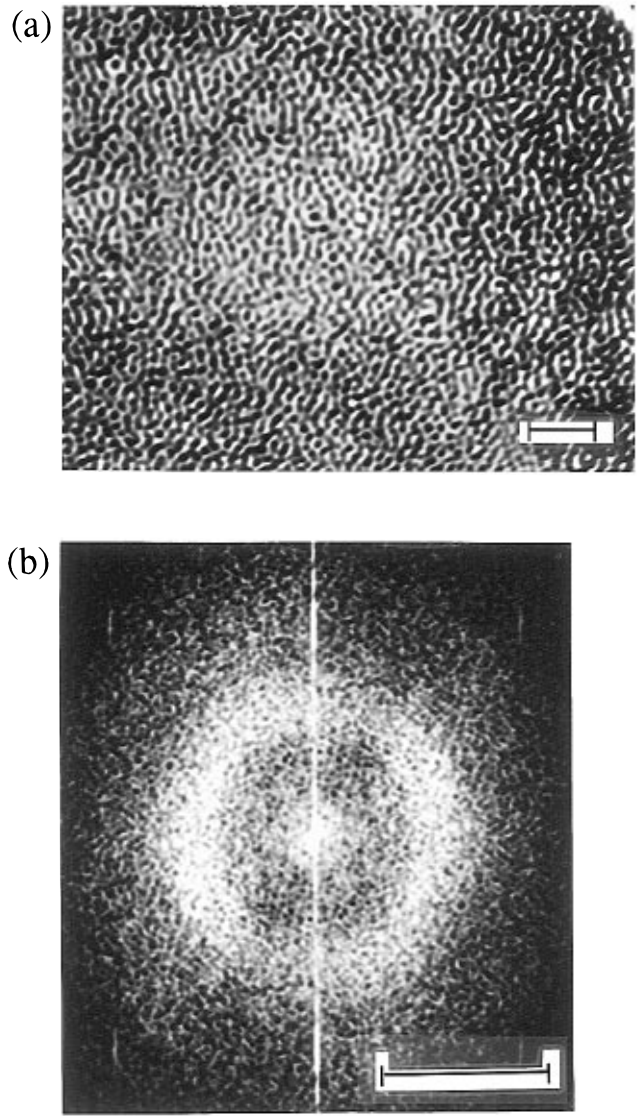

Figure 2. (a) Phase-contrast optical micrograph of a P(S-*stat*-CMS)/PVME (20/80) blend photo-cross-linked at 110 °C over 25 min. The scale corresponds to 10 μm. (b) Corresponding 2D-FFT power spectra. The scale is 5×10^4 cm^{-1}.

q_{max} is the position of the frequency corresponding to the maximum power spectra shown in Figure 2b. For the (20/80) blends, the characteristic length ξ of these structures increases with time in the early stage of irradiation and eventually approaches a constant value of 1.9 μm independent of reaction time, as depicted in Figure 3. Similar behavior was also observed for the other two compositions. It is worth noting that the reaction time where ξ reaches its equilibrium value depends on the composition. Namely, it is determined by the competitions between the growth of the spinodal decomposition process and the cross-linking reaction. Upon irradiation, the spinodal decomposition takes place as soon as the unstable region of the blend reaches the experimental temperatures. By using linear stability analysis, it has been shown that the growth of the unstable modes with long wavelengths is suppressed in the presence of chemical reactions[8] and only those with particular wavelengths are allowed to proceed. As a consequence, the pinning of the phase separation process might occur. Because the range of wavelengths of these unstable modes is controlled by the reaction kinetics, phase separation accompanied by chemical reactions provides an interesting wavelength-selection problem for polymer materials science.

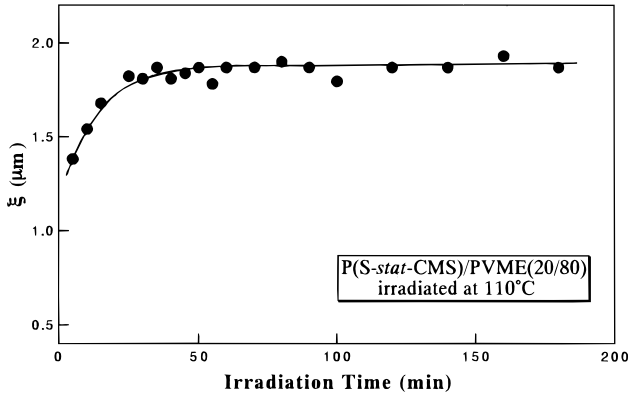

Figure 3. Irradiation time dependence of the bicontinuous structures in a P(S-*stat*-CMS)/PVME (20/80) blend photo-cross-linked at 110 °C over 25 min.

To test the scaling law proposed by Glotzer and coworkers, we rewrite eq 1 as

$$\xi(t)/t^{\alpha} = G(x) \tag{2}$$

Since the photo-cross-linking reaction approximately follows the first-order kinetics in the early stage of irradiation, the scaling variable $x = kt$ can be replaced by the irradiation time t. Therefore, the asymptotic behavior of the function $G(x)$ can be rewritten as

$$G(x) = \text{constant} \qquad \text{for } x \ll \infty$$

and

$$G(x) \propto t^{-\alpha} \qquad \text{for } x \to \infty \tag{3}$$

The left hand side of eq 2 is obtainable from experimental data provided that the exponent α for the growth of the morphology is known. Though the number of the data points in the region where ξ depends on irradiation time is not large, all the data obtained for the three compositions P(S-*stat*-CMS)/PVME (20/80), (50/50), and (70/30) can be reasonably fitted to the GDM scaling given by eq 2. The criterion for the fitting is choosing the exponent α in such a way that the quantity $\xi(t)/t^{\alpha}$ is independent of reaction time in the early stage of irradiation. Within the experimental errors, the prediction of the scaling function $G(x)$ is in good agreement with the experimental results. It was found that the exponent α of eq 2 varies from $^1/_5$ to $^1/_3$ with the blend composition. These results are illustrated in Figure 4 where $G(x)$ was plotted versus the reaction time t_{irr} in double logarithmic scale with $\alpha = {}^1/_5$ for (20/80), $^1/_4$ for (50/50), and $^1/_3$ for (70/30) blends. It is worth noting that the plots shown in Figure 4 exhibit a negative (positive) slope in the early stage of irradiation if a larger (smaller) value of α is taken for the fitting. Because the sample cloudiness and the increase in the glass transition temperature (T_g) of the blends prevent the photodimerization of anthracene, the phase separation kinetics is controlled by the gaps between the experimental temperatures and the T_g as well as the binodal line of the blends. The experimental results obtained above suggest that, in general, the phase separation process accompanied by photo-cross-linking reactions proceeds slower than the prediction of the Lifshitz−Slyozov−Wagner $t^{1/3}$ power law.[9,10] The results described above imply that eq 1 is quite universal and can be usefully applied to chemical systems under-

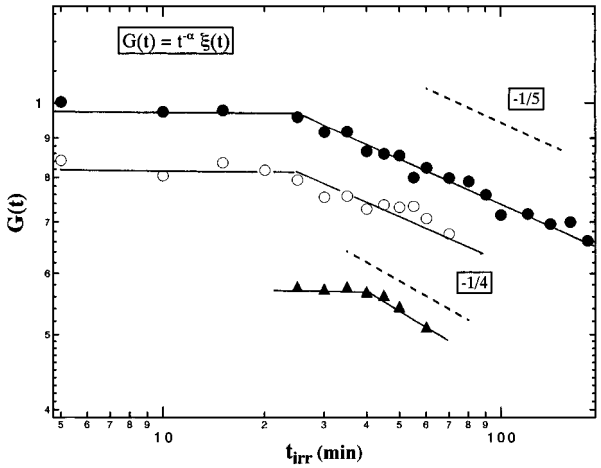

Figure 4. Experimental verification of the scaling law given in eq 1 for P(S-*stat*-CMS)/PVME (●) (20/80), $\alpha = 1/5$, (○) (50/50), $\alpha = 1/4$, and (▲) (70/30), $\alpha = 1/3$.

going phase separation with constraints such as cross-linking. On the other hand, the coarsening kinetics with the power $1/4$ has been proposed for the phase separation in the case of weak segregation, i.e. the regime where the interfacial thickness is comparable to the average domain size.[11] It is worthwhile to note that the GDM scaling law with $\alpha = 1/4$ was also held for the phase separation kinetics of binary polymer blends photo-cross-linked during the spinodal decomposition process.[12]

In summary, we have experimentally verified the scaling law proposed by Glotzer and co-workers by using photo-cross-linkable polymer blends. The scaling prediction for the temporal behavior of the intensity of the power spectra was not considered here because of the inaccuracy associated with the absolute intensity obtained by 2D-FFT of the optical micrographs. As mentioned earlier, the morphological evolution of photo-cross-linked blends shown here is the result of the competitions between two antagonistic effects, i.e. short-range attraction (activation) and long-range repulsion (inhibition). The former comes from the phase separation, and the latter originates from both the cross-linking reaction and the elastic strain associated with the network formation. It has been shown that the competitions between these two contradicting interactions are the origin of the formation of various ordered structures, i.e. the so-called modulated phases, which have been observed in a wide range of physical as well as chemical systems.[13] We think that photo-cross-linked polymer blends are also the chemical system having the capability of exhibiting modulated phases. Further experiments are currently being carried out in order to elucidate the roles of these competitions in the phase separation process of reactive polymer blends.

Acknowledgment. This work is supported by the Ministry of Education, Science, and Culture, Monbusho, Japan, via Grant-in-Aid No. 07651109. We thank Dr. Sharon C. Glotzer (Center for Theoretical and Computational Materials Science, National Institute of Standards and Technology, Gaithersburg, MD) for helpful discussion and communications. The technical assistance of Toshikazu Tamai (currently with Dynik Inc., Otsu, Japan) in the polymer synthesis is also gratefully acknowledged.

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