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Immobilization of Transient Structures in Polystyrene/Poly(2-chlorostyrene) Blends Undergoing Phase Separation by Using Photo-Cross-Linking

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ABSTRACT: Immobilization of the transient phase-separated structures during the spinodal decomposition process in the polystyrene/poly(2-chlorostyrene) blend is demonstrated by taking advantages of photo-cross-linking via photodimerization of anthracene moieties chemically attached to polystyrene chains. For this purpose, anthracene-labeled polystyrene (PSA)/poly(2-chlorostyrene) (P2CS) blends of composition (41.4/58.6) were jumped from the one-phase region into the spinodal region and were subsequently irradiated by UV light from a high-pressure mercury (Hg) lamp (365 nm) and a XeF excimer laser (351 nm). During the time evolution of the spinodal decomposition, cross-linking between different segments of PSA takes place via intermolecular photodimerization of anthracene groups. By dielectric measurements, it is found that there is a remarkable difference in tan δ between these irradiated blends and another of the same composition carried out without UV irradiation under the same thermal conditions. The morphology of the blend irradiated by a Hg lamp shows that the spinodal-like structures were partially immobilized, whereas these specific structures were frozen efficiently upon irradiation with a XeF excimer laser. These preliminary results reveal the possibility of designing new polymer blends with ordered structures in the range of micrometers by photo-cross-link.

Physical properties of polymer blends strongly depend on their structures at the molecular level resulting from the phase separation process. It is expected that immobilization of the transient structures in polymer blends undergoing a phase decomposition process would provide materials with unique properties due to the spatial concentration distributions of both component polymers. In fact, the time evolution characteristics of these transient structures determined by the kinetics of phase decomposition processes have been extensively investigated in recent years.[1-5] For the lower critical solution temperature (LCST) type polymer blends which undergo phase separation upon heating, the simplest way to immobilize these transient phase-separated structures is quenching quickly the blend undergoing phase separation at high temperatures to temperatures much lower than the glass transition temperatures of both components. However, the molecular structures obtained in this way are not permanently fixed due to the molecular motions in the vicinity of T_g and, particularly, to the polymer chain diffusion at high temperatures. Consequently, it is difficult to investigate the structure/properties relationships in these frozen materials.

In this paper, we would like to report some preliminary experimental results on immobilization by photo-cross-linking the transient structures in polystyrene/poly(2-chlorostyrene) blends obtained by temperature jump (T-jump) from the one-phase region into the spinodal unstable region. The cross-linking is achieved by taking advantages of intermolecular photodimerization of anthracene groups[6] chemically attached on polystyrene chains upon UV irradiation.

The structures of the component polymers are shown in Figure 1. Anthracene-labeled polystyrene (PSA, $M_w = 140\,000$, $M_w/M_n = 1.9$) is prepared by Williamson synthesis from chloromethylated polystyrene and 9-anthracenemethanol (Aldrich, recrystallized) by the procedure described previously.[7] The average labeling ratio for polystyrene is 11 anthracene groups per chain. Poly-

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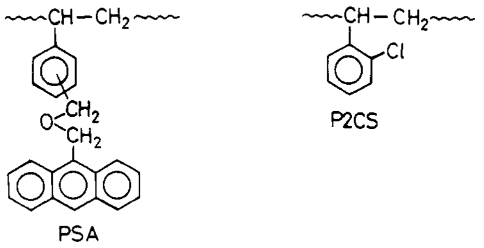

Figure 1. Structures of anthracene-labeled polystyrene (PSA) and poly(2-chlorostyrene) (P2CS).

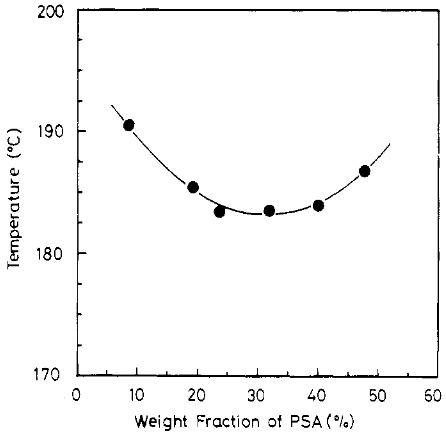

Figure 2. Cloud point curves of PSA/P2CS blends used in this experiment.

(2-chlorostyrene) (P2CS, M_w = 84,000, M_w/M_n = 2.3) is prepared by radical polymerization with α,α'-azobis(isobutyronitrile) (AIBN) as initiator and benzene as solvent at 60 °C. The blends of PSA and P2CS are obtained by casting benzene solutions of the polymer mixtures and are dried under vacuum at 140 °C over four nights prior to the experiments. Samples prepared in this way have a thickness of ca. 70 μm and are transparent at room temperature.

The phase separation behavior of PS/P2CS blends is of the LCST type and, recently, the existence of critical double points has been also proposed for this particular blend.[8,9] Namely, both the UCST (upper critical solution temperature) and the LCST can exist in PS/P2CS blends, depending on molecular weight. For anthracene-labeled polystyrene and poly(2-chlorostyrene) blends used in this study, the LCST behavior was observed. The cloud points of the blends of particular molecular weights in this experiment observed by light scattering are shown in Figure 2.[10] All the blends used in this experiment show a single T_g as observed by DSC but exhibit two peaks, corresponding to the T_g of component polymers, after heating to 200 °C, confirming that PSA and P2CS are miscible at room temperature.

To immobilize the transient structures generated during the phase separation process, a PSA/P2CS blend with the composition of 41.4/58.6 (sample no. 1) was jumped from the one-phase region (166.9 °C) into the spinodal region (192.8 °C).[11] At first, UV irradiation using light of wavelengths mainly at 365 nm from a high-pressure 250-W mercury (Hg) lamp (USH-250, Ushio Co., Japan) starts at 5 min (the time required for the sample to reach thermal equilibrium) after the temperature jump. Thus the sample was exposed continuously to UV irradiation for 30 min at 192.8 °C. After irradiation, the blend is cooled down to room temperature (25 °C, 8 °C/min). The degree of photo-cross-link resulting from photodimerization between anthracene groups on polystyrene chains is estimated from the variation in absorbance of anthracene before and after irradiation. For 30 min of irradiation, it is found that 21.5% of anthracenes have reacted. To confirm the effects of photo-cross-linking on the transient structures generated during the spinodal decomposition process, experiments using another two blends of the same composition were carried out under different conditions. One blend (sample no. 2) was submitted to exactly the same experimental conditions (for temperature jump and cooling down) as blend no. 1, without irradiation. The other one (sample no. 3) is an as-casted blend with experience of neither T-jump nor irradiation. Since these three blends (no. 1–3) are brittle, the characterization by mechanical experiments was not available for the particular molecular weights used in this study. Consequently, dielectric measurements[12] were performed with these three different samples for comparison. It was found that the tan δ of these three samples are remarkably different. As an example, temperature dependence of tan δ of these three samples obtained at 150 Hz is shown in Figure 3.

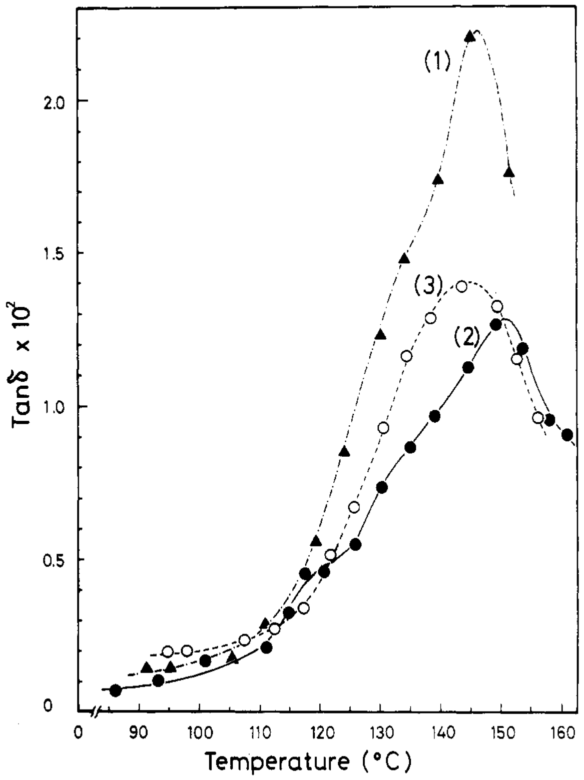

Figure 3. Temperature dependence of tan δ of PSA/P2CS (41.4/58.6) blends irradiated by a Hg lamp: (1) T-jump and irradiation; (2) T-jumped in the dark; (3) as-casted blend.

For the blend no. 3 (as-casted blend), there exists only one maximum at 145 °C, which corresponds to the α-relaxation process of the blend due to the compatibility of the two polymers. Similar results for PS/P2CS blends have been reported previously by Alexandrovich et al.[13] Blend no. 2 (T-jumped in the dark) shows one maximum at a higher temperature, 151 °C, and shoulders at ca. 132 °C and ca. 117 °C due to the phase separation of anthracene-labeled PS and P2CS during 30 min after the T-jump in the dark. On the other hand, tan δ of blend no. 1 that experienced both T-jump and UV irradiation shows a shoulder at around 134 °C and a maximum at 146 °C, which is close to the maximum of the compatible blend (no. 3) but looks somewhat shifted toward the high-temperature side. Though the values of tan δ are relatively small, it seems that the dielectric relaxation behavior, as revealed by the positions of a maximum and shoulders, of blend no. 1 that experienced both T-jump and UV irradiation is in between those of the miscible (blend no. 3)

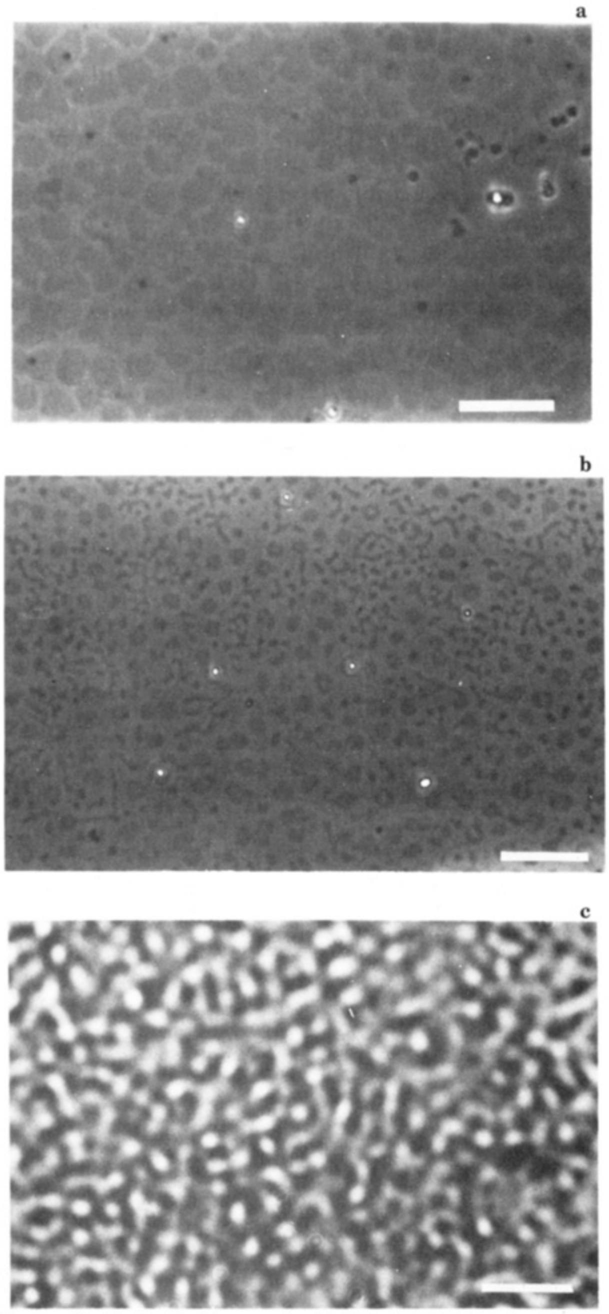

Figure 4. Optical micrograph of PSA/P2CS blends obtained under the same thermal condition: (a) T-jumped in the dark; (b) T-jumped and irradiated by Hg lamp in 30 min; (c) T-jumped and irradiated by XeF excimer laser in 5 min. The scale is 20 μm for parts a and b and 10 μm for part c.

and the phase-separated sample (blend no. 2). Similar behavior of tan δ of these three blends is also observed at other frequencies (30, 300, 600, and 900 Hz).

To confirm the effects of UV irradiation on the transient structures in PSA/P2CS blends undergoing phase separation via the spinodal decomposition process, the morphology of blend no. 2 (T-jumped in the dark) and blend no. 1 (T-jumped with irradiation) was observed by using a phase-contrast optical microscope (Nikon Model XF-Ph-21, Japan). These results are shown in Figure 4. As expected, the two-phase structures composed of various nuclei of different sizes due to the phase separation process were observed in blend no. 2, as shown in Figure 4a. On the other hand, the mixtures of the two-phase structures and the spinodal-like structures were observed in blend no. 1 as shown in Figure 4b. The sizes of nuclei in the two-phase structures of blend no. 1 are much smaller than those seen in blend no. 2. These results imply that during 30 min at 192.8 °C, blend no. 2 was completely phase separated, whereas under the same condition, the cross-links which occurred between PSA chains in the blend no. 1 partially immobilized the spinodal structures generated by the T-jump. Consequently, a part of such the spinodal structures still remains after irradiation as observed under an optical microscope. In fact, the morphology of blend no. 1 (T-jumped and UV irradiated) is determined by the competition between the two opposite driving forces: the disentanglement process of P2CS chains, which try to diffuse away from the PSA cross-linked networks, and the cross-linking process, which is determined by the rates of the network formation caused by the photo-cross-linking between PSA chains. During the time evolution of the phase decomposition, the former process favors the two-phase structure formation, whereas the later tends to maintain the spinodal structures. By irradiation with a Hg lamp, it is obvious that the former process overcomes the later, and consequently, the immobilization of the transient structures during the phase separation process is not efficient. Therefore, instead of a Hg lamp, a XeF excimer pulse laser was used as a light source to induce the cross-linking between PSA chains. For this purpose, another blend (sample no. 4) of the same composition (41.4/58.6) was used. Immobilization was carried out with a XeF excimer pulse laser (Lambda Physik, Model EMG101-MSC, 15-ns pulse width). The wavelength used for the irradiation is 351 nm and the intensity per one pulse is ca. 7 mJ/cm^2. The T-jump conditions for blend no. 4 are exactly the same as those described above except that after the T-jump, UV light from the laser was impinged on the sample for only 5 min. Blend no. 4, after irradiation, was kept at 192.8 °C for another 25 min before cooling down to room temperature in order to keep the thermal history of this sample in the same condition as that for blend no. 1 (irradiated by a Hg lamp). The variation in absorbance of anthracene attached to PS chains was 21.4% after irradiation. The morphology of this blend observed by a phase-contrast optical microscope after irradiation with an excimer laser is shown in Figure 4c. At first, it is obvious that the spinodal-like structures of blend no. 4 are revealed in the order of micrometers. It was noted that these specific structures were observed throughout the sample. Since the photo-cross-linking, which was confirmed by the decrease in absorbance of anthracene groups, occurs in the spinodal region, this result implies that by using a strong UV light source such as an excimer pulse laser, the transient structures during the phase separation process via spinodal decomposition can be efficiently immobilized in a short period of time (5 min). The corresponding tan δ of blend no. 4 obtained by dielectric relaxation is shown in Figure 5. It is found that the temperatures at which a maximum and shoulders appear in the tan δ of blend no. 4 are very close to those obtained in blend no. 1 (irradiated by a Hg lamp). However, it is much broader. This broadness probably comes from the small difference in the concentration gradients of component polymers in the modulated structures, as revealed by the corresponding morphology shown in Figure 4c.

Very recently, by using γ-ray irradiation[14a] and chemical cross-linking[14b] in the one-phase region, Briber and Bauer have shown the effects of crosslinking on the phase separation behavior of polystyrene/poly(vinyl methyl ether) blends. It is worth noting that the difference between cross-linking by γ-ray irradiation and photo-cross-linking

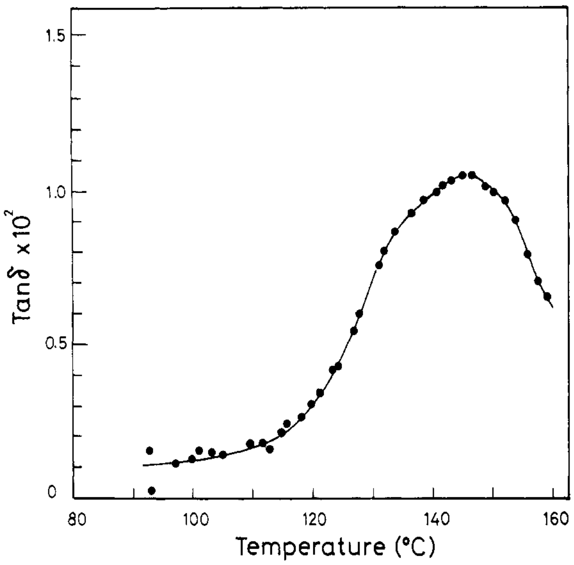

Figure 5. Temperature dependence of tan δ of a PSA/P2CS (41.4/58.6) blend (sample no. 4) after T-jump and irradiation for 5 min with a XeF excimer laser.

is essential. By using photo-cross-linking between photosensitive groups attached on component polymers, the three different types of cross-links in binary blends of polymer A and polymer B (i.e., A–A, B–B, and A–B) can be carried out selectively. By doing so, the immobilization of the transient structures during the phase separation process might provide polymeric materials with completely different physical properties, corresponding to each type of cross-link. The experimental results presented here are an example of one of these three types.

So far, we have shown that by taking advantage of photodimerization of anthracene, it is possible to immobilize the transient structures of polystyrene/poly(2-chlorostyrene) blends during the phase decomposition process. By UV irradiation using a mercury lamp, the spinodal structures can be partially immobilized only since the long period of time is required to achieve the effective cross-link density. On the other hand, by using a strong light source such as an XeF excimer pulse laser, the spinodal structures during the phase separation process can be efficiently immobilized as demonstrated. The experimental data reported in this paper are the preliminary results on controlling the morphology of polymer blends by taking advantages of photo-cross-link reactions. The results described above show the possibility for a new route to design polymer materials with the periodic structures in the range of micrometers. We think that the physical properties of these new blends with ordered structures are of great interest for practical purposes. Furthermore, since the formation of a new phase composed of a cross-linked component is possible in the system where the cross-link density reaches a certain critical value, photo-cross-linking of polymer chains in polymer blends undergoing phase separation might provide some new morphology resulting from the effects of chemical reactions. Further experiments are in progress in order to elucidate the effects of cross-link density as well as the effects of different types of cross-links on the morphology and corresponding physical properties of these new blends.

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(10) The heating rate for this experiment is 0.2 °C/min.
(11) The spinodal region was judged from the growing behavior with time of the scattering intensity observed at a fixed angle from the blends submitted to the temperature jump. It is found that for a particular composition of PSA/P2CS (41.4/58.6), above 189 °C, the scattering intensity grows exponentially with time: the typical scattering behavior due to the growing of the concentration fluctuations in the spinodal region. Below this temperature, the scattering intensity levels off quickly after a small linear growth.
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