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Structure of Polymer Blends Photo-Cross-Linked during the Spinodal Decomposition Process

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ABSTRACT: Anthracene-labeled polystyrene/poly(2-chlorostyrene) blends (PSA/P2CS) with the composition 40/60 were photo-cross-linked during the time evolution of the spinodal-decomposition process. Photo-cross-links were carried out by utilizing the intermolecular photodimerization reaction between anthracene groups that were chemically attached on polystyrene chains (*Macromolecules* 1989, 22, 2107). The structure and property of these photo-cross-linked blends were examined by means of optical microscopy and dielectric relaxation. It was found that, upon irradiation with a XeF excimer laser, the ordered structures resulting from a temperature-jump (T-jump) from the one phase into the spinodal region were efficiently frozen. For a constant duration time of irradiation (5 min), the sizes of these ordered structures become larger as the blend was photo-cross-linked at a later time. Furthermore, the ordered structures revealed in these irradiated blends are different from those experiencing the same T-jump condition without irradiation. The corresponding maxima of the dielectric tan δ's of these irradiated blends shift toward the higher temperature side as the delay time of irradiation increases. Though only PSA chains were cross-linked, these ordered structures are thermally quite stable.

I. Introduction

Synthesis and characterization of polymeric materials with ordered structures in the range of submicrons are the research subjects to which extensive works have been devoted in the past decades.[1] Block copolymers are typical materials that reveal such ordered structures due to the microphase separation occurring between chemically different components. For block copolymers, the sizes of various ordered structures resulting from the microphase separation are limited in the range of submicrons, whereas the equilibrium phase-separated structures in polymer blends are usually larger than microns. From the standing point of materials science, it is expected that the physical properties of polymers can be greatly modified if one can efficiently control the morphology of polymer blends. For this purpose, there are so many studies that have been carried out to understand the static as well as the kinetic aspects of phase-separation processes in polymer blends.[3,4] It is known that, depending on thermodynamical conditions, polymer blends can undergo phase separation via two distinctly different processes, in principle. One is the nucleation and growth process, and the other is the spinodal-decomposition process.[2] These processes resemble those that have been found in metallic alloys in the past decades.[5] The spinodal-decomposition process, which is characterized by the spatially periodic concentration fluctuation, has attracted a lot of attention due to its uniqueness. From the practical viewpoint, it is of great importance if polymers with controllable ordered structures can be designed. Perhaps the simplest way to achieve these purposes is to freeze the ordered structures developing at different stages of the spinodal-decomposition process by quenching the blend undergoing phase separation from the spinodal region into the corresponding glassy regime. However, this method is severely limited due to the reversible motions of polymer chains, which take place in the vicinity of the glass transition temperature, T_g. Therefore, permanent freezing of these ordered structures is highly expected. Recently, a few experiments including our preliminary work[6] have been performed in an attempt to freeze the spinodal structures of polymer blends. Those include the kinetic studies on the phase-separation behavior of chemically reactive mixtures of nitrile rubber and epon where the cross-link reactions between polymer segments are spontaneously induced by heating.[7] Reactions between cross-linkers and polymer segments were also carried out in an attempt to freeze the concentration fluctuation developing during the spinodal-decomposition process in polybutadiene/polyisoprene blends.[8] Since temperature strongly affects both the kinetics of the phase-separation processes and the cross-link reactions, it turns out that control of the time evolution of the spinodal-decomposition process is not easily accessible by thermally induced reactions. Therefore, to achieve this purpose, it is desirable to utilize an external field that is independent of thermodynamical variables such as pressure, volume, and/or temperature. Thus, the light-induced cross-link reaction is probably one of the most promising candidates for these purposes since not only can photochemical reactions provide the fast way to cross-link polymer chains but the specific cross-linked sites on polymer chains can also be selected by labeling the polymer components with suitable photoreactive groups.

In the previous report,[6] we have demonstrated that it is possible to freeze the modulated structures resulting from the spinodal-decomposition process of polystyrene and poly(2-chlorostyrene) (P2CS) blends by utilizing the intermolecular photodimerization reaction between anthracene moieties that are chemically attached on polystyrene chains (PSA). In this paper by using photo-cross-links, control of the morphology of polymer blends undergoing the spinodal-decomposition process, which develops at different stages after a temperature-jump (T-jump), is described in more detail. At first, the effects of irradiation on the structure and property of these photo-cross-linked blends are investigated by using optical microscopy and the dielectric relaxation method. Furthermore, the thermal stability of these photo-cross-linked blends was also examined in order to evaluate the efficiency of the A–A cross-links for this particular blend. On the other hand, a polymer blend irradiated during the time evolution of the phase-decomposition process is actually a thermodynamically open system where the formation of

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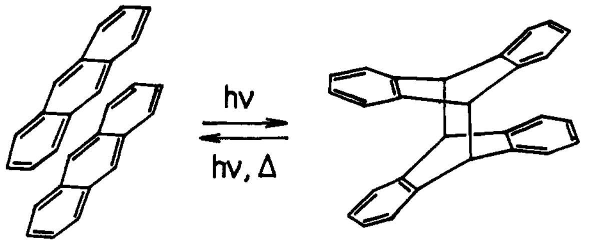
Scheme I
Intermolecular Photodimerization of Anthracenes



a microstructural self-organization is highly possible under specific conditions. Accordingly, the possibility for a light-induced instability in irradiated polymer blends is finally discussed in terms of the reaction-diffusion dynamics of physical systems deviated from thermodynamical equilibrium.[9]

II. Experimental Section

(1) **Materials.** Polymers used in this experiment are the same as those reported previously.[6] Polystyrene (M_w = 140 000, M_w/M_n = 1.9) was obtained from the rough fractionation of a commercially available sample (Wako Chemical Industries, Japan) using methanol and benzene. Chloromethylation of this fractionated polystyrene was carried out according to the conventional method using chloromethyl methyl ether (Wako) and dichloromethane mixtures as solvent and zinc chloride (Nakarai, Japan) as catalyst.[10] To avoid the cross-link reaction that might occur during the chloromethylation, polymer concentrations were kept at less than the overlap concentration, C^*, of the reaction solutions. Anthracene-labeled polystyrene (PSA) was prepared by coupling anthracenemethanol (Aldrich, recrystallized in toluene) with chloromethylated polystyrene in dried dimethylformamide (DMF) by following the modified Williamson method in the presence of sodium hydride at room temperature as described previously.[11] The labeling ratio of anthracene-labeled polystyrene prepared this way is ca. 11 anthracene groups per chain. Poly(2-chlorostyrene) was prepared by radical polymerization of the corresponding monomer in benzene at 60 °C with α,α'-azobis(isobutyronitrile) (AIBN) as an initiator. The composition of PSA/P2CS blends used in this work was kept at 40/60 (PSA/P2CS). These blends were prepared by casting benzene solutions of the polymer mixtures and were dried at 140 °C over 4 nights to remove solvent and oxygen prior to the experiments. PSA/P2CS blends prepared in this way have a thickness of ca. 70 μm and are transparent at ambient temperatures. The diameter of these samples is ca. 1.5 cm.

As shown in Scheme I, upon irradiation with UV light (λ = 365 nm), anthracene groups attached on PSA chains photodimerize and result in a semi-IPN of PSA and P2CS as schematically represented in Figure 1.

(2) **Light Source and Irradiation Procedure.** Since the morphology resulting from photo-cross-links of polymer blends is determined by the competition between the growth rates of the phase-separation process and the cross-link reaction rates, using fast light pulses is required to control efficiently the morphology of these blends. In the previous report, we have demonstrated that the spinodal structures of these PSA/P2CS blends can be frozen efficiently by irradiation with a UV pulse laser.[6] Therefore, in this work the same XeF excimer pulse laser (351 nm; Lambda Physik Model EMG101-MSC) was used to induce photo-cross-link reactions. UV light of 15 ns in pulse width was impinged on the blends with the repetition rate of ca. 10 Hz. The average intensity per pulse is 7 mJ/cm^2, and the total time for irradiation is 5 min. The small fluctuation of the laser intensity that sometimes occurs was compensated by adjusting the repetition rate so that the total intensity input into the blends is constant in 5 min of irradiation. By this compensation, the fluctuation of the light source probably does not seriously affect the phase-separated structures resulting from cross-links, since the diffusion of polymer chains is very slow in the bulk state.

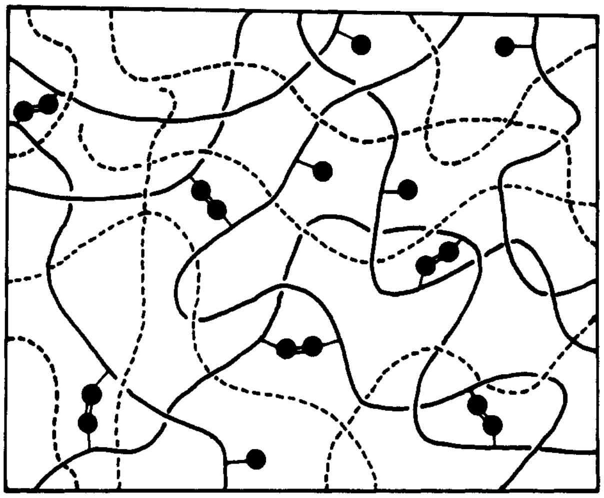


Figure 1. Schematical representation of the semi-IPN formation due to the A–A type photo-cross-link: (—) PS; (- - -) P2CS; (●) anthracene; (●═●) photodimer of anthracene.

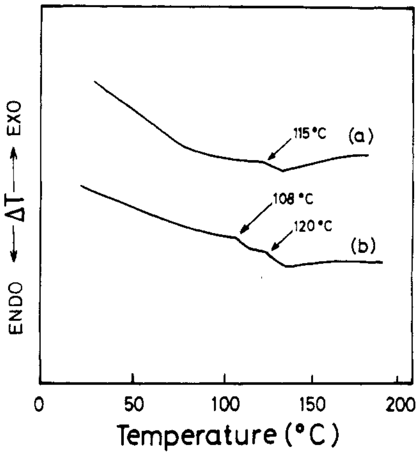


Figure 2. DTA thermograms of PSA/P2CS (40/60) blends obtained with the heating rate 10 °C/min: (a) first run; (b) second run.

(3) **Phase Separation Behavior of PSA/P2CS Blends.** The phase separation of PSA/P2CS (40/60) blends was examined by DTA (Thermal Analyzer System, Shimadzu DT-30, Japan) and light scattering. As depicted in Figure 2a, the thermogram of an as-cast PSA/P2CS (40/60) blend exhibits a single glass transition temperature, T_g, at 115 °C obtained with the heating rate 10 °C/min. This temperature is in between the T_g's of anthracene-labeled polystyrene (105 °C) and that of poly(2-chlorostyrene) (125 °C) obtained under the same experimental conditions (10 °C/min). However, after heating to 200 °C, this blend reveals two glass transition temperatures (108 and 120 °C) as shown in Figure 2b. This result, which is consistent with the cloud-point data obtained by light scattering, indicates that the phase-separation behavior of PSA/P2CS blends is of the LCST (lower critical solution temperature) type.

(4) **Characterization of Irradiated Blends.** After irradiation under various conditions, PSA/P2CS blends were cooled to ambient temperature (25 °C, 8 °C/min). The cross-link densities of these irradiated blends were determined from the changes in optical density at the first absorption peak (389 nm) in the long wavelength side of the absorption spectra by using a UV–visible spectrophotometer (Shimadzu Model UV-160). The morphology of the blends irradiated under different conditions was observed under a phase-contrast optical microscope (Nikon Model XF-NTF-21) equipped with a Normarski prism. The images of irradiated blends observed under a phase-contrast optical microscope are transferred to a digital image analysis system (LA-525, Pias Co. Ltd., Japan) for the Fourier transform operation to obtain the two-dimensional power spectra of the corresponding morphology. On the other hand, since irradiated

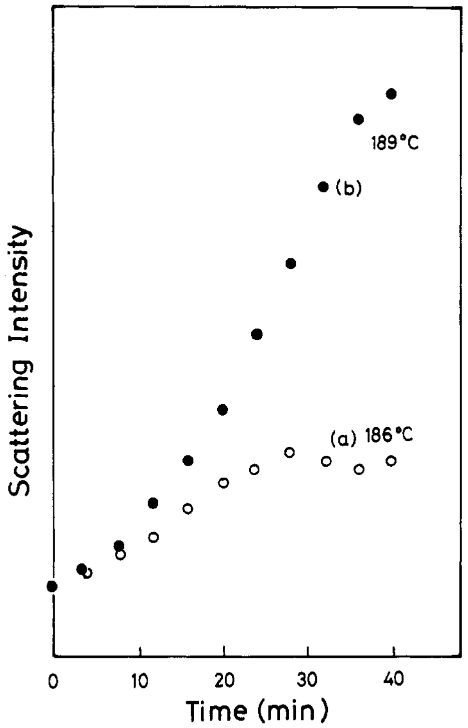


Figure 3. Time evolution of the light scattering intensity observed at 22°: (a) jumped from 172 to 186 °C; (b) jumped from 172 to 189 °C.

PSA/P2CS blends are brittle, the characterization of their mechanical properties by a conventional rheometer was not available. Instead, dielectric tan δ's of these samples in the range 30–900 Hz were measured by using the dielectric relaxation method as reported previously.[12]

(5) Temperature-Jump Experiments. The spinodal region of PSA/P2CS (40/60) blends used in this work was qualitatively determined by monitoring the time evolution of the scattering intensity at a fixed angle (ca. 20°) under different temperature-jump depths. From the prediction of the Cahn–Hilliard theory,[13] the scattering intensity grows exponentially with time for the initial stage of the spinodal-decomposition process. This theoretical prediction has been experimentally verified for a number of polymer mixtures of high molecular weights.[14-17] In Figure 3 is shown the time evolution of the scattering intensity from the PSA/P2CS (40/60) blends that were submitted to a temperature-jump from 172 °C (one-phase region) to 186 °C (shallow jump), and to 189 °C (deep jump), respectively. The scattering intensity obtained after the shallow *T*-jump to 186 °C varies almost linearly with time, whereas it grows exponentially for the case of the deep jump. These results qualitatively indicate that, at least, 189 °C is located inside the spinodal region of this particular PSA/P2CS system. Therefore, to ensure that the blends after a *T*-jump are actually located inside the spinodal region, 192.8 °C was chosen as the temperature at which irradiation experiments are undertaken for this particular composition (40/60 PSA/P2CS). Though the detail of kinetic studies on the phase-separation process was not carried out at this moment, this temperature, i.e., 192.8 °C, is actually located inside the spinodal region of this 40/60 blend, as verified by the morphological result obtained by quickly quenching the blend from 192.8 to 0 °C. This experimental result will be described in detail later.

III. Results and Discussion

(1) Effects of the Delay Time of Irradiation on the Resulting Morphology. In order to elucidate the effects of cross-links on different stages of the spinodal-decomposition process, the duration time for irradiation was fixed at 5 min, while the starting times for irradiation were set at 5, 15, and 25 min after the *T*-jump. For convenience, these irradiated samples are denoted as blend nos. 1–3, respectively. By irradiating in this way, the cross-link densities in these blends that are determined by the duration time of irradiation can be kept at a constant value. The irradiation procedure is shown in Figure 4. The morphology of blend nos. 1–3 corresponding to these irradiation conditions is shown in Figure 5a–c. These pictures reveal the spatially periodic structures of these irradiated blends. As an example, the 2-dimensional power spectrum of blend no. 2 obtained from the Fourier transform of the corresponding morphology by using the technique of digital image analysis is shown in Figure 5d. As seen in Figure 5a–c the more the blend is irradiated at later times after the *T*-jump, the interconnecting structures become larger. To elucidate the effects of photo-cross-links on the conventional spinodal structures, another PSA/P2CS (40/60) blend (sample no. 4) was submitted to the same *T*-jump condition as blend no. 2 (irradiated in 5 min at 15 min after jump) and was subsequently quenched to 0 °C (iced water) at 15 min after jump without irradiation. As shown in Figure 6, the morphology of this unirradiated and quenched sample shows the conventional bicontinuous structures, which are much larger than those obtained for blend no. 2. It is worth noting that these two blends experience the same thermal history except that blend no. 2 was irradiated with UV light and blend no. 4 was performed in the dark. These results indicate that photo-cross-links have frozen the ordered structures developing during the spinodal process of PSA/P2CS blends and, at the same time, do affect the formation of these spinodal structures. Consequently, the decrement in sizes of the bicontinuous structures resulting from photo-cross-links is not only caused by the suppression of P2CS chains diffusion, but the formation of PSA networks during the spinodal-decomposition process is also responsible for this modification. On the other hand, the morphology of the PSA/P2CS blend, which was irradiated in 5 min at 25 min after the *T*-jump, seems to exhibit a kind of higher ordered structures, which are apparently different from those obtained by irradiation at the earlier time, i.e., 5 and 15 min after the *T*-jump. Such higher ordered structures are also revealed by a light scattering profile with multiple higher order maxima for a PSA/P2CS blend that was irradiated by a XeF excimer laser after being submitted to a shallower *T*-jump (from 166 to 185 °C).[18]

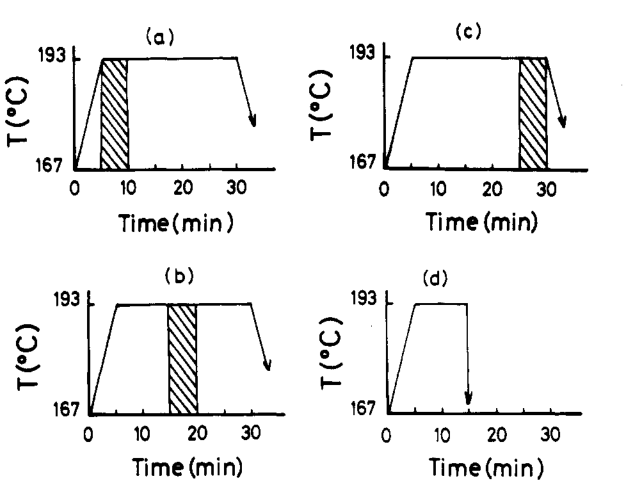


Figure 4. Irradiation procedure for blend nos. 1–4: (a) blend no. 1; (b) blend no. 2; (c) blend no. 3; (d) blend no. 4 without irradiation.

(2) Dielectric Relaxation of Photo-Cross-Linked Blends. The dielectric tan δ's of these irradiated samples (blend nos. 1–3) are shown in Figure 7. Though the duration time for irradiation was kept constant (5 min), the maximum of tan δ of irradiated blends shifts toward the higher temperature side as irradiation starts at a later

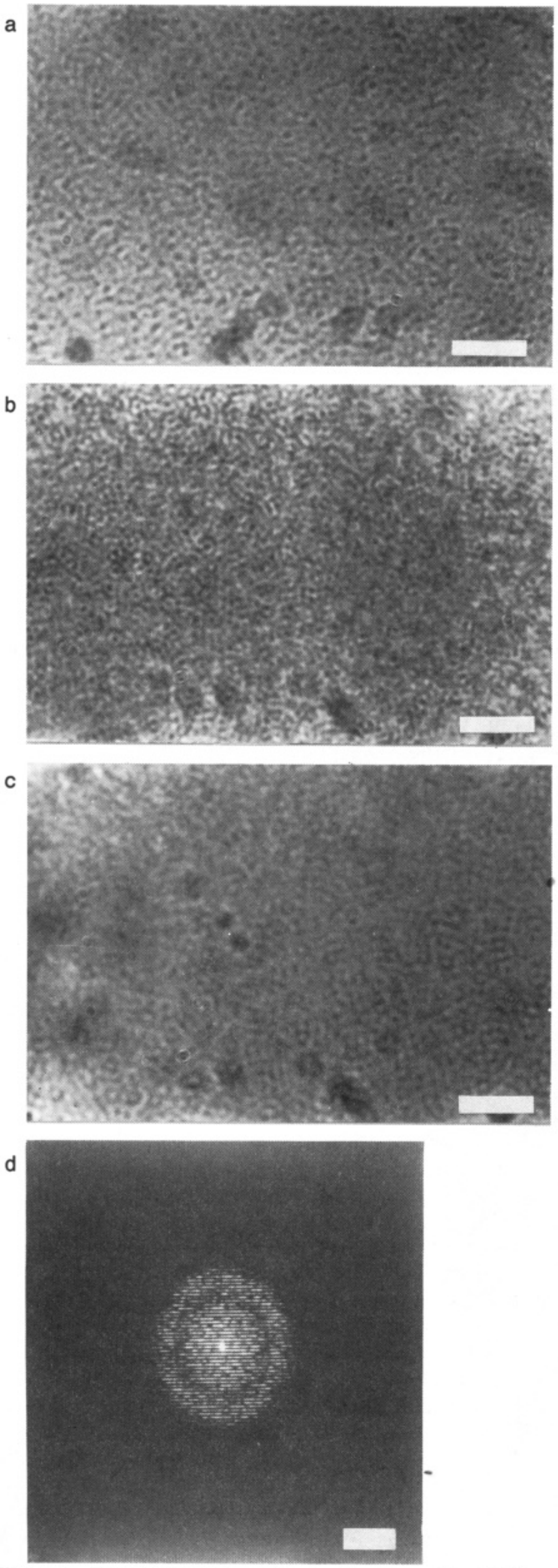


Figure 5. Effects of delaying the starting time of irradiation on the morphology of PSA/P2CS (40/60) blends: (a) blend no. 1, irradiated at 5 min after the *T*-jump; (b) blend no. 2, irradiated at 15 min; (c) blend no. 3, irradiated at 25 min. The duration of irradiation is 5 min for all blends. The scale is 10 μm. (d) Power spectra of blend no. 2 obtained by two-dimensional Fourier transform. The scale corresponds to 4.8 × 10^4 cm^{-1}.

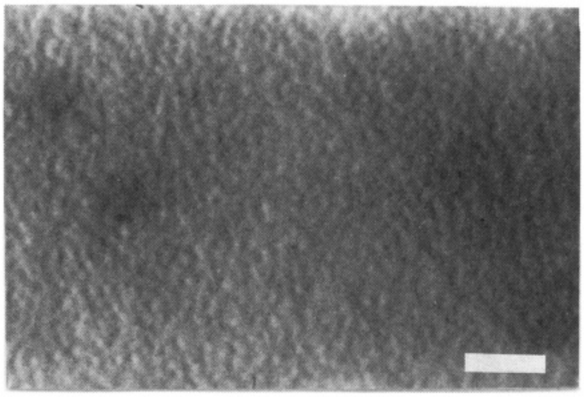


Figure 6. Morphology of a PSA/P2CS blend (no. 4) obtained by quickly quenching to 0 °C after jumped and allowed to stay in the dark at 192.8 °C for 15 min. The scale is 10 μm.

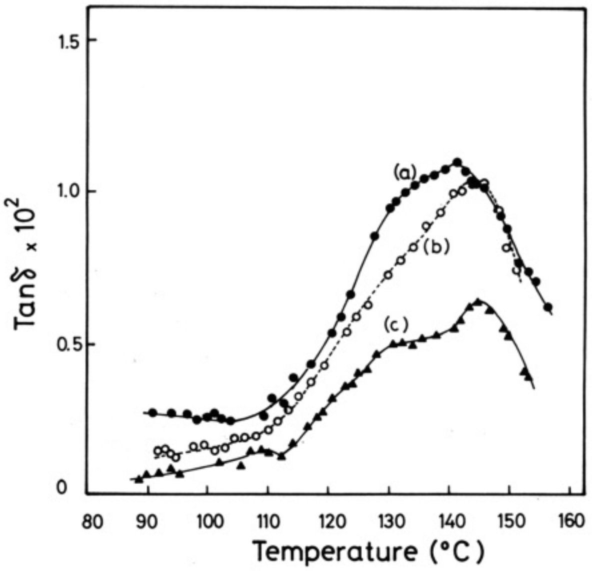


Figure 7. Dielectric tan δ's of photo-cross-linked blends: (a) blend no. 1 irradiated at 5 min after the *T*-jump; (b) blend no. 3 irradiated at 25 min after the *T*-jump; (c) a blend with two-phase structures. All were measured at 30 Hz, and the time for irradiation is 5 min.

time. On the other hand, as shown in the same figure, for the blend irradiated in 5 min at 25 min after the *T*-jump, the maximum in tan δ of this particular sample approaches that of the blend with two-phase structures that was obtained by holding the blend at 193 °C in the dark. The cross-link densities of all irradiated blends after 5 min of irradiation are in the range 25–30% as estimated from the change in optical density of anthracene groups before and after irradiation. Since the total number of photons input into these samples was almost the same in 5 min of irradiation, these irradiated blends should have the same cross-link density. Consequently, the difference in the temperature dependence of tan δ observed under different irradiation conditions is essentially originated from the ordered structures shown in Figure 5 rather than coming from the increment of the glass transition temperatures due to cross-links. By comparison with the results on morphology shown in Figure 5, these dielectric relaxation data imply that dielectric tan δ becomes less sensitive to the concentration fluctuations in irradiated blends as the sizes of these ordered structures grow to some extent. Therefore, the thermal stability of these photo-cross-linked blends was only evaluated for blend no. 1, which was irradiated in the early time (5 min) after the *T*-jump. These experimental results are subsequently discussed in the next section.

(3) Thermal Stability of Photo-Cross-Linked Blends. Since only polystyrene chains were cross-linked

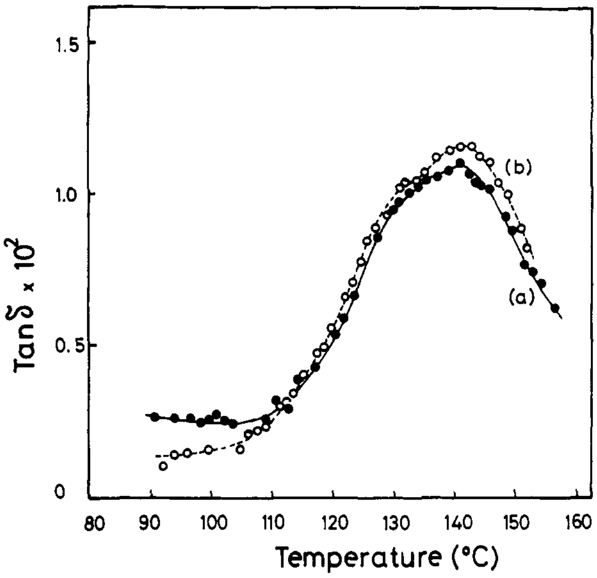


Figure 8. Effects of heating on the dielectric tan δ of blend no. 1 irradiated in 5 min at 5 min after jump: (a) before heating; (b) after heating to 190 °C for 2 h. All were measured at 30 Hz.

in this experiment (A–A cross-links), the resulting polymer networks are of the semi-IPN (interpenetrating polymer network) type. It is of interest to examine the thermal stability of the ordered structures in these semi-IPN's upon heating. For this purpose, blend no. 1, which was irradiated by laser in 5 min at 5 min after the T-jump, was reheated at 190 °C for 2 h and was cooled to ambient temperature prior to another run of dielectric measurements. Figure 8 shows the tan δ of the irradiated blend before annealing (a) and of the corresponding annealed sample (b). Though this sample was heated at a temperature much higher than the T_g's of both components, the temperature dependence of tan δ is almost unchanged. This result implies that the concentration fluctuations in PSA/P2CS blends were actually frozen by the cross-link reactions beween PSA chains. This fact is due to the extremely slow diffusion of P2CS chains trapped in the cross-linked networks of PSA chains. These experimental data show the evidence that, by utilizing the A–A photo-cross-links, binary polymer blends with various ordered structures in the range of micrometers can be designed.

(4) On the Possibility for the Existence of a Structural Self-Organization Process in Light-Irradiated Blends. As shown in parts a–d of Figure 5, the structures, which result from photo-cross-links of PSA/P2CS blends during the spinodal-decomposition process, are spatially periodic. However, the morphology of these irradiated samples is quite different from that of a PSA/P2CS blend, which was quenched to temperature much below T_g after experiencing the same T-jump condition in the dark. The morphology obtained in this work strongly suggests that the cross-links of PSA chains have modified the conventional spinodal structures via the network formation of PSA chains. Recently, the phase stability of weakly cross-linked polymer networks has been theoretically investigated by Binder and Frisch.[19] In their theory, by addition of the contribution of the elastic terms due to the network formation to the Flory–Huggins free energy, the effects of cross-links on the phase boundary of a polymer blend were examined. Experimentally, the variation of the spinodal lines of semi-IPN of polystyrene and poly(vinyl methyl ether) at different cross-link densities has been demonstrated by using small-angle neutron-scattering (SANS)[20,21] and temperature-jump light scattering.[22] Since the kinetic effects become very prominent as the cross-link densities increase, the determination of the spinodal temperatures of the cross-linked samples based on the extrapolation of the infinite correlation length or to the zero-mutual diffusion coefficient is difficult for samples with high degrees of cross-link density.

In order to explain the modification of the spinodal structures by photo-cross-links, it is necessary to take into account the competition between the cross-link reaction rates and the polymer chain diffusion. The formation of the ordered structures resulting from photo-cross-links during the time evolution of the spinodal-decomposition process evolves in two stages. At the first stage, these ordered structures are formed under the thermodynamic nonequilibrium state since the blend is an open system during irradiation. In general, for irradiated blends there also exists a gradient of the light intensity between the front and the back sides of the sample. This intensity gradient, which is determined by the thickness and the molecular extinction coefficient of the sample at the wavelength of irradiation, is stationarily sustained during the time of irradiation. At this stage, the time dependence of the concentration of polymer segments can be described by the reaction-diffusion kinetics[23] where the diffusional process of polymers strongly couples to the concentration fluctuation via photochemical reactions. The second stage of the structure formation in photo-cross-linked blends begins after the light is turned off. Here the nonequilibrium structures, which were generated during the time of irradiation, tend to relax toward the equilibrium state. This relaxation process strongly depends on the destination temperatures of the T-jump, which activate the diffusional processes of the un-cross-linked P2CS chains, and depends also on the degree of cross-links of PSA chains, which tend to suppress the phase separation. The more the cross-linking process between PSA chains proceeds, the more the phase-separation process in the system is accelerated. However, at the same time, the mobility of polymer chains is more suppressed. Eventually, the final morphology of irradiated blends is determined by the balance of these two competitive processes. At this moment, we think that there are two possibilities for these particular ordered structures. One is coming from the spinodal structures with multiple wavelengths due to the inhomogeneous distribution of the photo-cross-link reactions taking place in the blend upon irradiation. The other is originated from the onset of a structural self-organization process since the experiments described here fulfill the necessary conditions for the reaction-diffusion kinetics. In order to elucidate the effects of photo-cross-links on the morphology of polymer blends undergoing phase separation, more elaborate experiments and quantitative analysis of the ordered structures resulting from different irradiation conditions as well as from different types of photo-cross-link reactions (A–B, A–A and B–B) are currently in progress. These results will be reported in the near future.

IV. Summary

The structure and property of anthracene-labeled polystyrene (PSA)/poly(2-chlorostyrene) (P2CS) blends, which were cross-linked by irradiation with UV light, have been shown. The following results were obtained:

(1) The ordered structures resulting during the spinodal process have been efficiently frozen by taking advantage of intermolecular photodimerization of anthracene groups labeled on PS chains.

(2) After a temperature-jump into the spinodal region, for a constant cross-link density, the resulting ordered

structures become larger and the maximum of the dielectric tan δ gradually shifts toward that of the blends with two-phase structures upon delaying the starting time of irradiation.

(3) Semi-IPN's obtained by photo-cross-links in this work are thermally quite stable. Both the morphology and dielectric tan δ results indicate that, in principle, it is possible to control the morphology as well as the corresponding physical properties of polymer blends by photo-cross-link reactions.

(4) Photo-cross-links between polymer chains in polymer blends undergoing phase separation have the potential to provide a new type of molecular composites with a variety of controllable morphology.

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