Semi-Interpenetrating Polymer Networks Prepared by *in Situ* Photo-Cross-Linking of Miscible Polymer Blends

Toshikazu Tamai, Akira Imagawa, and Qui Tran-Cong*

Department of Polymer Science and Engineering, Kyoto Institute of Technology, Matsugasaki, Sakyo-ku, Kyoto 606, Japan

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ABSTRACT: Semi-interpenetrating polymer networks (semi-IPN) of styrene–(chloromethyl)styrene copolymer (P(S-*stat*-CMS)) and poly(vinyl methyl ether) (PVME) were prepared by *in situ* photo-cross-linking of miscible P(S-*stat*-CMS)/PVME (50/50) blends. To selectively cross-link the P(S-*stat*-CMS) component, the CMS segments of this copolymer were chemically labeled with anthracene. Upon irradiation at 365 nm, anthracene undergoes photodimerization and induces network formation of P(S-*stat*-CMS) chains in the blend. The miscibility as well as the morphology of the resulting semi-IPN critically depends on the competition between the cross-linking reaction kinetics and the polymer diffusion driven by thermodynamic instabilities accompanying the reaction. Photo-cross-linking of P(S-*stat*-CMS) at a temperature close to the glass transition region of the blend provides a transparent semi-IPN with a broad T_g. On heating, these semi-IPNs undergo phase separation. The phase domains are restricted to the nanometer scale as revealed by small-angle X-ray scattering. The phase-separated semi-IPNs exhibit iridescence when obtained during the photo-cross-linking reaction carried out in the one-phase region close to the binodal temperature. Phase-contrast optical microscopy combined with digital image analysis showed that these particular semi-IPNs possess lamella-like structures in the micrometer scale. These preliminary results indicate that multiphase polymers with a wide variety of controllable ordered structures ranging from the nanometer to micrometer scale can be obtained by using *in situ* photo-cross-linking of miscible polymer blends.

Interpenetrating polymer networks (IPN) belong to a class of molecular composites where the two different polymer networks are chemically prepared in a way such that they interpenetrate without covalent bondings.[1] Over the past decades, IPNs have been an attractive research subject because it is expected that the specific topological network structures of IPNs could provide polymer materials with physical properties such as high toughness or excellent damping. In most cases, phase separation occurs during the synthesis and as a result, polymers with two-phase structures are obtained during the preparation. The reason for this phase separation is polymer chain diffusion driven by the thermodynamic instabilities which dominates the rate of network formation. These instabilities arise from both a decrease in entropy of mixing and an increase in elastic free energy.[2] Consequently, in the synthesis where both or either of the starting components are monomers, the phase separation occurs and the final products exhibit two-phase structures.

Several experiments have been performed in an attempt to obtain single phase full- as well as semi-IPNs. In these studies, solutions containing either a prepolymer and a monomer or two prepolymers in the presence of their appropriate cross-linkers were heated to induce cross-links between polymer chains. Eventually, IPNs were obtained by removing the solvent upon heating. Such procedures have been employed to prepare a number of IPNs.[3,4] Recently, semi-IPNs between polystyrene and poly(vinyl methyl ether) (PVME) were prepared by using cross-linkers which are attached to polystyrene chains via copolymerization.[5] These experiments share a common feature in that the cross-linking is initiated by thermally activated reactions. From the viewpoint of kinetics, it is of great interest to prepare IPNs from miscible polymer mixtures using photo-cross-linking. Photochemical reactions are advantageous both because the rate of cross-link reactions can be controlled by adjusting the light intensity and/or cross-linker contents and because the reactions can be induced at temperatures below the glass transition of the blends. Furthermore, the cross-link kinetics can be easily monitored during the reaction process because the absorption spectra of photo-cross-linkers are usually located in the wavelength region where most of the components of polymer blends are transparent.

In this paper, we report preliminary results of semi-IPNs prepared by *in situ* photo-cross-linking of miscible poly(styrene-*stat*-(chloromethyl)styrene)/poly(vinyl methyl ether) (P(S-*stat*-CMS)/PVME) blends. The cross-linking was performed by photodimerization of anthracene moieties covalently attached to the P(S-*stat*-CMS) chains.[6] Photosensitive P(S-*stat*-CMS)/PVME (50/50) blends were cross-linked in the one-phase region under two extreme conditions. One was carried out in the one-phase region close to the glass transition temperature (T_g) of the blends and the other in the vicinity of the phase boundary. Semi-IPNs obtained after cross-linking were characterized by differential scanning calorimetry (DSC), phase-contrast optical microscopy combined with digital image analysis, and small-angle X-ray scattering (SAXS).

To efficiently adjust the content of anthracene labels on the polystyrene (PS) chains, (chloromethyl)styrene was copolymerized with styrene in benzene at 60 °C over 5 days. The resulting copolymer P(S-*stat*-CMS)[7] with $M_w = 2.6 \times 10^5$ and $M_w/M_n = 1.5$ measured by GPC using standard polystyrenes as reference was then reacted with the potassium salt of 9-anthracenecarboxylic acid in anhydrous dimethylformamide at 65 °C over 8 h.[8] Note that the composition of CMS is 15 mol % of the copolymer as obtained from elemental analysis. The anthracene label content is ca. 120 anthracenes/chain as measured by UV spectroscopy. Subsequently, the anthracene-labeled P(S-*stat*-CMS) (P(S-*stat*-CMS)-

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* To whom correspondence should be addressed.

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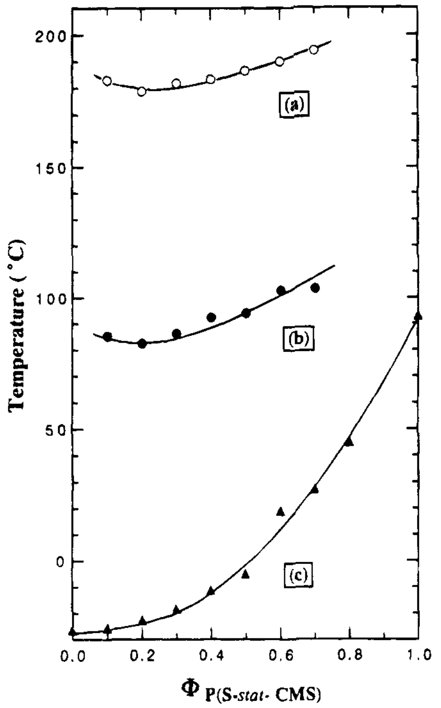

Figure 1. Composition dependence of the cloud points of the unlabeled P(S-*stat*-CMS)/PVME blend (a) and the anthracene-labeled P(S-*stat*-CMS)-A/PVME blends (b) and composition dependence of the T_g of the P(S-*stat*-CMS)-A/PVME blends (c).

A) was blended with PVME (Aldrich, $M_w = 9.6 \times 10^4$, $M_w/M_n = 1.8$, precipitated twice using *n*-heptane/methanol mixtures) by casting the benzene solutions containing appropriate amounts of the two polymers. All the samples described were dried at 60 °C over 3 nights prior to the experiments. The blends are sandwiched between two glass plates with a 50 μm spacer used to control the sample thickness. The glass transition temperatures (T_g) of these blends were measured by using differential scanning calorimetry (Mac Science, Model 3100) with a heating rate of 5 °C/min. The cloud points were determined by light scattering, and morphology analysis was carried out with a phase-contrast optical microscope (Nikon, Model THX-21) equipped with a digital image analyzer (Pias, Model LA-525, Japan).[9] Small-angle X-ray scattering using synchrotron radiation was carried out at the Photon Factory, Synchrotron Radiation Facilities (National Laboratory for High Energy Physics, BL-10C beam line, Tsukuba, Japan). X-rays with a wavelength of 1.488 Å selected from a 2.5 GeV storage ring were point focused on the 1D position-sensitive photon counter.[10]

All the anthracene-labeled P(S-*stat*-CMS)/PVME blends used in this work exhibit a single glass transition temperature, indicating that the two polymers are miscible. Figure 1 shows the composition dependence of T_g and the cloud points of the P(S-*stat*-CMS)/PVME and P(S-*stat*-CMS)-A/PVME blends. These cloud points were obtained after extrapolating the data to zero heating rate in order to avoid kinetic effects due to the large difference in the T_gs of the two polymers. P(S-*stat*-CMS)-A/PVME blends possess a lower critical solution temperature (LCST) resembling the well-known polystyrene/poly(vinyl methyl ether) (PS/PVME) mixtures. Compared to the unlabeled blends, the cloud points of P(S-*stat*-CMS)-A/PVME shift more than 80 °C toward the low-temperature side, indicating that labeling P(S-*stat*-CMS) with ca. 5 mol % of anthracene significantly reduces the miscibility of the blend. Similar effects of labeling on the phase behavior of polymer blends have been observed previously for poly(2-chlorostyrene)/poly(vinyl methyl ether) blends.[10] In this paper, only P(S-*stat*-CMS)-A/PVME blends with the composition 50/50 were used for the cross-link experiments. Irradiation was carried out in the one-phase region under two extreme experimental conditions by using a Hg–Xe lamp (500 W, Hamamatsu Photonics, Japan), at ambient temperature (30 °C), about 30 °C above the T_g of this particular composition, and at 80 °C, i.e., about 14 °C below the extrapolated cloud point. The main wavelength for irradiation was 365 nm and the corresponding intensity was 3 mJ/(cm^2·s). Irradiating this blend over 400 min at 30 °C results in a transparent blend with a broad T_g observed by DSC as shown in Figure 2. However, upon heating at 70 °C over 15 h in vacuo, this photo-cross-linked P(S-*stat*-CMS)-A/PVME (50/50) blend exhibits two distinct T_gs as shown in the same figure, indicating that phase separation has taken place. Under this experimental condition, 60% of the anthracenes on the P(S-*stat*-CMS)-A chains has photodimerized as calculated from the decrease in absorbance of anthracene. This is equivalent to an average of 36 cross-link junctions per chain. These results imply that the network formed by the cross-linked P(S-*stat*-CMS)-A chains has trapped the PVME chains and suppressed the phase separation. This conclusion is also supported by the SAXS profiles shown in Figure 3, where the SAXS scattering curves of three P(S-*stat*-CMS)-A/PVME (50/50) blends obtained under different experimental conditions are illustrated. These profiles have been appropriately shifted along the ln $S(q)$ axis for comparison. For an as-cast blend (a) and the blend irradiated at 30 °C over 400 min (b), except in the very low q range, the scattering profile is almost the same. However, as seen in Figure 3c, a small shoulder located at $q = 0.04$ Å^{-1} appears when the cross-linked blend (b) is annealed at 70 °C over 15 h in vacuo. This result is consistent with the T_g data shown in Figure 2, suggesting that the diffusion of un-cross-linked PVME chains which were trapped inside the networks of P(S-*stat*-CMS)-A created by the photo-cross-linking at 30 °C is activated upon heating over a long time and that these chains diffuse very slowly from these networks to form microdomains in the semi-IPN. To observe this time evolution process in more detail, a (PS-*stat*-CMS)-A/PVME (50/50) blend photo-cross-linked under the same conditions as the sample (b) was jumped from 30 °C, i.e., the cross-link temperature, into the unstable region of the blend (120 °C). The time evolu-

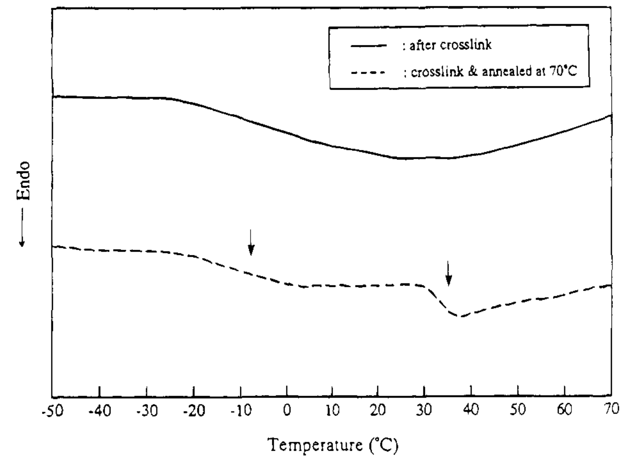

Figure 2. DSC thermograms of P(S-*stat*-CMS)-A/PVME (50/50): (—) after cross-linking at 30 °C over 400 min; (– – –) after cross-linking and annealing at 70 °C over 15 h under vacuum.

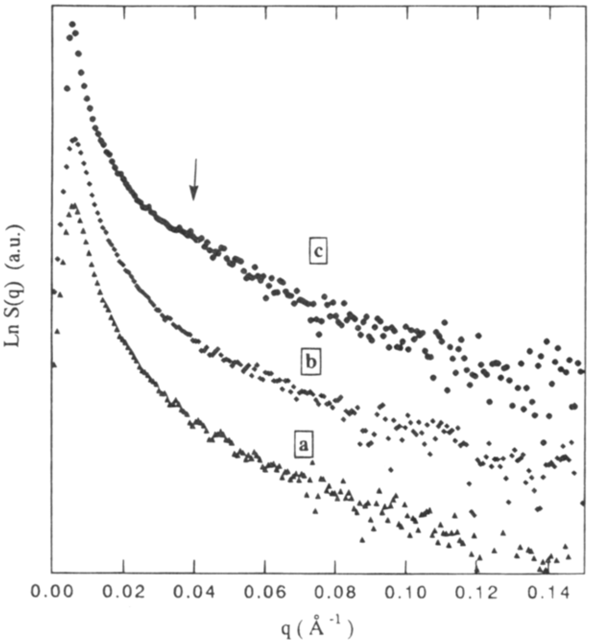

Figure 3. SAXS profiles of P(S-*stat*-CMS)-A/PVME (50/50) blends: (a) as-cast; (b) after cross-linking; (c) after cross-linking and annealing under the conditions shown in Figure 2. For comparison, these curves have been appropriately shifted along the $S(q)$ axis.

tion of the structures was monitored by time-resolved small-angle X-ray scattering. It was found that the scattering intensity of the shoulder at $q = 0.04$ Å^{-1} increases with time and eventually reaches an equilibrium value at 20 min after the T-jump. On the other hand, the position of the shoulder was almost unchanged with time. By assuming that all the cross-link junctions formed by the photodimerization of anthracenes are homogeneously distributed in the blend and that the P(S-*stat*-CMS)-A chains exist in the sample in their unperturbed dimension, the average mesh size of the networks was roughly estimated as 85 Å. This value is smaller than the Bragg spacing 160 Å, which corresponds to the shoulder at 0.04 Å^{-1} as calculated from the X-ray wavelength. Furthermore, since the shoulder still exists after quenching the sample to room temperature and particularly since the blend after cross-linking shows two separated T_gs as seen in Figure 2, this shoulder does not come from a correlation of the cross-linked blend but rather correlates to the microphase separation in the semi-IPN. From the above results, we conclude that photo-cross-linking of miscible polymer blends at a temperature close to T_g leads to the formation of metastable semi-IPNs. Upon heating the cross-linked sample in the two-phase region, phase separation takes place when the un-cross-linked component PVME gains enough activation energy to overcome the barrier created by the surrounding networks. Depending on the photo-cross-linking kinetics and the network structures, this phase decomposition process can be restricted to the nanometer scale.

Another example demonstrating the competitions between cross-linking reaction kinetics and thermodynamic instabilities is shown for the case where a P(S-*stat*-CMS)-A/PVME (50/50) blend is irradiated in the vicinity of the phase boundary. Upon irradiation over 150 min at 80 °C, i.e., 14 °C below the cloud point, the blend undergoes phase separation and unexpectedly exhibits iridescence. Figure 4a shows the corresponding morphology of this photo-cross-linked blend. This morphology looks like the "spinodal" structures with the white and the black domains representing respectively PVME-rich (un-cross-linked component with lower refractive index) and P(S-*stat*-CMS)-rich (cross-linked component with higher refractive index) phases. The one-dimensional powder spectra obtained from the 2D fast Fourier transform (FFT) of this optical micrograph are shown in Figure 4b, exhibiting a broad peak at ca. 1.48×10^4 cm^{-1}, which corresponds to a Bragg spacing of 4.2 μm in Figure 4a. There also exist several concentric domains in the morphology shown in Figure 4a which are not clear enough to be revealed by the FFT analysis. However, as shown in Figure 5, these peculiar structures become obvious as a P(S-*stat*-CMS)-A/PVME (50/50) blend with a lower label content, i.e., about 65 anthracenes/chain, was irradiated over 600 min at 90 °C. Note that this temperature is 40.5 °C below the cloud point of this particular blend. The optical micrograph clearly exhibits the concentric phase-separated domains which resemble the so-called target patterns often observed in systems far from equilibrium.[12] The presence of targets with different sizes in the blend indicates that the photo-cross-links were formed inhomogeneously in the irradiated sample. This conclusion is supported by the fact that the cross-linking monitored through the time dependence of the absorbance of anthracenes during irradiation in the one-phase region followed the Kohlrausch–Williams–Watts (KWW) kinetics.[11] The mechanism of the emergence of this

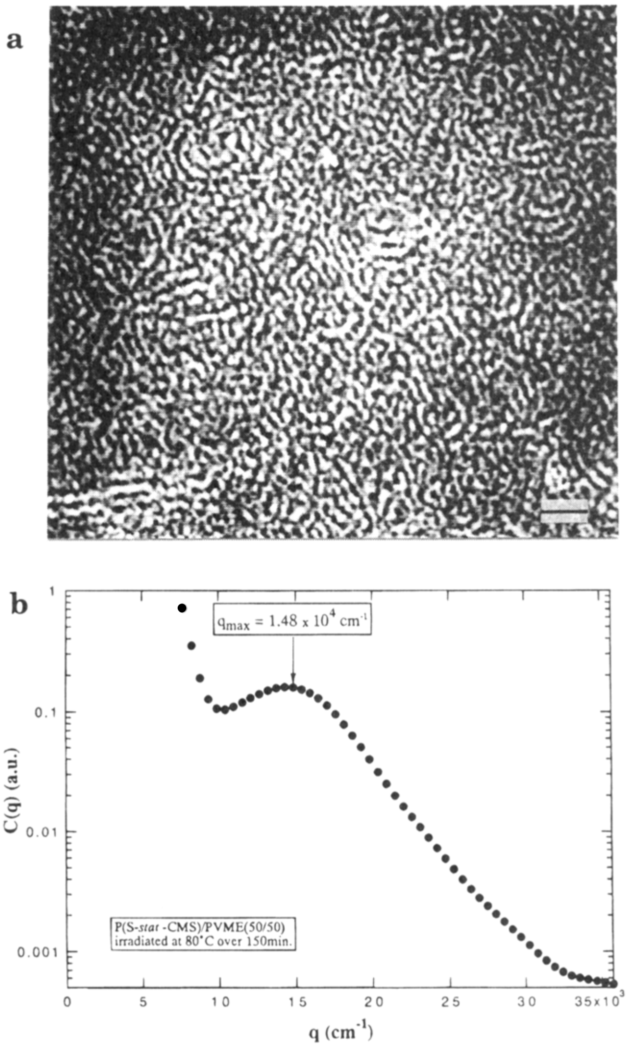

Figure 4. (a, Top) Optical micrograph of P(S-*stat*-CMS)-A/PVME (50/50) obtained after cross-linking at 80 °C over 150 min. The scale corresponds to 10 μm. (b, Bottom) The corresponding 1D power spectra obtained by FFT.

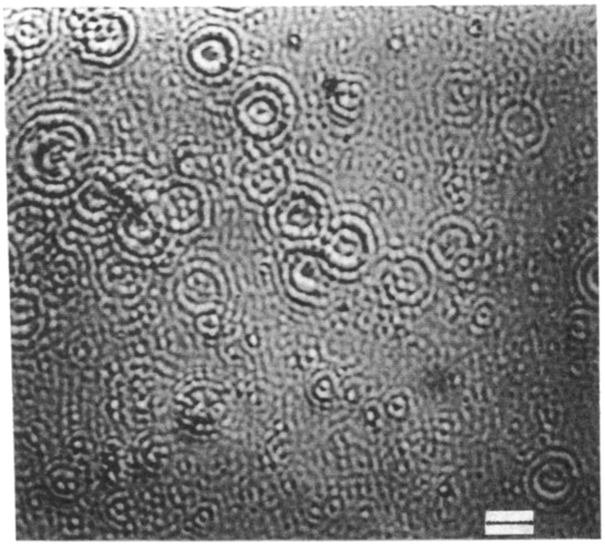

Figure 5. Optical micrograph of P(S-*stat*-CMS)-A/PVME (50/50) with lower anthracene label content (65 anthracenes/chain) irradiated at 90 °C over 600 min. The scale corresponds to 10 μm.

peculiar morphology is not well understood at this time. In general, photo-cross-linking of one polymer component in a binary polymer blend has two opposite effects on the resulting morphology. One is the modification of the free energy of mixing by the network formation and the other is the decrease in mobilities of both the cross-linked and the un-cross-linked components. The former favors phase separation whereas the latter tends to suppress it. There are two typical cases for these competing effects on the resulting morphology. For a blend with a lower critical solution temperature such as P(S-*stat*-CMS)-A/PVME, the coexistence curve shifts toward the low-temperature side on cross-linking. When the photo-cross-linking reactions are performed at high temperatures in the one-phase region, the phase separation takes place at an early stage of irradiation because the new coexistence curve reaches the experimental temperature. Under this condition, the diffusion of the un-cross-linked PVME chains overcomes the constraints of the networks and leads to a macrophase separation with domain sizes in the micrometer range. This is the case shown in Figures 4a and 5 for the P(S-*stat*-CMS)-A/PVME (50/50) blends irradiated at high temperatures (80 and 90 °C). The ordering of these phase-separated domains probably arises from the couplings between photo-cross-linking reactions and polymer chain diffusion. One of the control parameters for this ordering process is the temperature gap between the cloud point and the experimental temperature. Theoretically, these morphologies can be described by a set of Cahn–Hilliard equations[13] containing the cross-link reaction terms which are nonlinear with respect to the concentration of anthracenes. It was shown that rich ordered structures can emerge from such a reaction–diffusion mechanism.[14] On the other hand, upon cross-linking the sample at low-temperatures, particularly in the vicinity of the glass transition temperature, both polymer components are frozen before the new coexistence curve can reach the experimental temperature. Thermodynamically, though the mixture might be unstable under this condition, phase separation cannot take place due to kinetic effects. If the sample is brought to a temperature where the PVME chains are activated enough to diffuse away from the cross-linked P(S-*stat*-CMS) chains, phase separation will occur under the constraints of these networks and as a result, microphase separation is observed as depicted in Figure 3c. These conclusions are also supported by the average cross-link density γ of the P(S-*stat*-CMS) networks estimated from the changes in absorbance of anthracenes under these irradiation conditions. It was found that γ for the blends cross-linked at 30 °C over 400 min is ca. 36 junctions/chain, which is much higher than the cross-link densities obtained by irradiation at high temperatures shown in Figure 4a(ca. 8 junctions/chain) and Figure 5 (ca. 13 junctions/chain). In general, when photo-cross-links of a binary polymer mixture are produced at different temperatures, the mesh size distribution of the networks would be different even if the blends have the same average cross-link density because the polymer diffusion and the reaction kinetics are affected by the concentration fluctuations.[15] This can be demonstrated by combining the photo-cross-link kinetics with the scattering data analysis using appropriate model functions. On the other hand, elaborate experiments such as the continuous monitoring of the development of the morphology emerging during irradiation as well as annealing after cross-linking are necessary to elucidate the mechanism for the emergence of the target patterns shown in Figure 5. Besides this ordering process, *in situ* photo-cross-linking of miscible polymer blends also has the potential of providing multiphase polymer materials with controllable ordered structures ranging from the nanometer to micrometer scale. Such experiments are currently in progress and will be reported later.

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