Spinodal decomposition induced by cross-linking reaction in a binary polymer mixture

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SUMMARY: Phase separation of a binary polymer mixture of poly{styrene-co-[p-2,2,2-trifluoro-1-hydroxy-1-trifluoromethylthyl-α-methylstyrene]} (PS(OH)) and poly[(methyl methacrylate)-co-(glycidyl methacrylate)] (PMMA(G)) upon cross-linking reaction was studied using time-resolved light scattering (TRLS) and optical microscopy. The blends of PS(OH)/PMMA(G), in which PMMA(G) containing 1.4 mol-% epoxy groups can be selectively cross-linked with the multifunctional agent 4,4'-methylenebis(α-chloroaniline) (MOCA) and PS(OH) contains 1.8 mol-% of the strongly proton-donating group –C(CF3)2OH, exhibit a lower critical solution temperature (LCST). The cross-linking reaction was carried out for two compositions of PS(OH)/PMMA(G)/MOCA, 50/50/0.7 and 40/60/0.8 (w/w/w), at various temperatures located in the one-phase region between the coexistence curve and the glass transition temperature of the blends. TRLS investigation shows that the phase separation takes place via spinodal decomposition (SD) induced by the increase in the molecular weight of PMMA(G) during the cross-linking reaction. A modulated phase structure with the characteristic features of periodicity and dual connectivity of the phases was developed in this case. The dynamics of SD were investigated in terms of changes of the peak scattering vector q_m(t) as a function of time. They are dependent on the reaction temperature and composition. A scaling relation q_m(t) \propto t^{-f(x)} describing the behavior of the evolution of phase separation upon reaction was supported by the experiments.

Introduction

Spinodal decomposition induced by a temperature jump from the one- into the two-phase region in the multicomponent polymer systems has been extensively investigated by experiments, theory and computer simulations, due to its importance from a purely scientific viewpoint as well as in the design and control of structures and properties. SD is an unstable and spontaneous process that occurs owing to the instability at an infinite-solubility composition fluctuation. As a result of SD, a characteristic morphology can be fixed or frozen by quenching the demixed system below the glass transition temperature (T_g) after an appropriate period of phase separation.

However, in practice the phase separation of polymer mixtures often proceeds under the presence of an external field such as a chemical reaction, a temperature gradient, or a shear flow. In particular, phase separation accompanied by a chemical reaction has been of great interest because it is strongly related to the toughness of cross-linked epoxy resins etc. For example, in a thermoset/thermoplastic blend the components are usually mixed together and the cross-linking of the epoxy resin occurs in situ. Assuming that the blend is initially miscible, the increase of the molecular weight of the epoxy resin during curing may result in a phase separation, even if the temperature is kept constant, due to the decreasing entropy of mixing of the epoxy component. The SD nature of the reaction-induced phase separation in such systems has been revealed by light-scattering studies, and the regularly phase-separated structure was detected for the fully cured materials, which can be interpreted in terms of a structure formation mechanism via SD.

SD induced by a reaction proceeds isothermally, but the thermodynamic driving force for a phase separation characterized by quench depth, i.e. the temperature difference between the LCST (or UCST) and the reaction temperature, increases with time. Simultaneously, the mobility of the components decreases during the reaction. These two contributions cause that the dynamics of SD induced by a reaction are quite different from the conventional SD process. The phase separation can be frozen eventually by the cross-linking of the mixtures. It is rather natural that the resultant morphology in this particular case is strongly dependent on the dynamics of phase separation and the rate of chemical reaction. However, the evolution of SD induced by chemical reaction and the effects of the reaction on the dynamics of phase separation are not completely understood yet, mainly due to the complex interaction between phase separation and cross-linking.

In this paper, we study the SD induced by the cross-linking reaction of a binary polymer mixture in which one com-
ponent can be selectively cross-linked with a multifunctional agent. The sample we use is a mixture of poly[styrene-co-\(p\-2,2,2\text{-trifluoro}-1\text{-hydroxy}-1\text{-trifluoromethylthyl-a-methylstyrrene}\)] (PS(OH)) and poly[(methyl methacrylate)-co-(glycidyl methacrylate)] (PMMA(G)). Among these, PS(OH) with the strongly proton-donating group \(-\text{C(CF}_3\text{)}_2\text{OH}\) shows the most remarkable effect on the miscibility with the carbonyl-containing polymer. For instance, for a typical immiscible blend system of polystyrene/poly(methyl methacrylate), only 2 mol-% of \(-\text{C(CF}_3\text{)}_2\text{OH}\) group already render the miscibility\(^9\). Hence, PS(OH)/PMMA(G) mixtures are expected to possess a lower critical solution temperature (LCST). PMMA(G) containing a small amount of epoxy groups was selectively cross-linked by utilizing a cross-linking agent sensitive to the epoxy groups. The cross-linking reaction was chosen to happen in the one-phase region located between the coexistence curve and the glass transition temperature of the blends. The phase separation is studied mainly by using time-resolved light scattering (TRLS) and optical microscopy. The dynamics of SD are discussed on base of the phase diagram of the PS(OH)/PMMA(G) mixture was obtained from optical microscopy (OM) observation. After the blend films on the cover glass were annealed at a given temperature for 24 h, some of the films became translucent and a phase-separated structure was observed under OM, from which we judged that the blend is in the two-phase region of the phase diagram. Since some other samples were still transparent and no indication of a phase separation was observed under OM, we judged that these blends are in the single-phase region. The single-phase nature was carefully confirmed by further annealing at the same temperature for 48 h. These annealing experiments were repeated with different isothermal settings.

We also prepared solution-cast films of the blend loaded with cross-linking agent in a similar manner. The content of cross-linking agent equals the stoichiometric equivalent of epoxy groups in the PS(OH)/PMMA(G) blend.

Light-scattering measurements during reaction were conducted on our home-made time-resolved light scattering (TRLS) apparatus. The principle of the apparatus was described in some earlier papers\(^{11}\); here we only mention the parts relevant to the present study. The light source is a 15 mW plane-polarized He-Ne laser with a wavelength of 632.8 nm. The sample sandwiched between two cover-glasses was inserted into a heating chamber kept at a constant temperature with an accuracy of \(\pm 0.1\) °C. The chamber was set horizontally on the light-scattering stage. Radiation from the He-Ne gas laser was applied vertically to the specimen. The light scattering profile \(I(q)\) (relative scattered intensity \(I\) versus scattering vector \(q\)) under a Vv (parallel polarized) optical alignment was determined using a two-dimensional CCD-camera detector with 512 \(\times\) 512 pixels and an intensity resolution of 256 levels. The magnitude \(q\) of the scattering vector \(q\), corresponding to the wave number of concentration fluctuation, is defined by

\[
q = (4\pi/\lambda) \sin(\theta/2)
\]

where \(\theta\) is scattering angle and \(\lambda\) the wavelength of the laser in the sample. The changes of the light scattering profile were recorded at appropriate time intervals during isothermal annealing (cross-linking reaction).

**Results and discussion**

**Phase separation by TRLS**

The phase diagram of PS(OH)/PMMA(G) blends solution-cast from chloroform is carefully examined by long-time annealing in our investigation. All solution-cast films of PS(OH)/PMMA(G) blends with different compositions after drying at 60 °C under vacuum are transparent and homogeneous under the optical microscope. The clarity is maintained even after annealing for 24 h for

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**Experimental part**

Poly[styrene-co-\(p\-2,2,2\text{-trifluoro}-1\text{-hydroxy}-1\text{-trifluoromethylethyl-a-methylstyrrene}\)] (PS(OH)) was synthesized as previously described\(^9\). PS(OH) used in this study contains 1.8 mol-% of hydroxyl groups, measured by means of a fluorine analysis and its weight-average molecular weight \(\bar{M}_w = 4.1 \times 10^4\) measured by gel permeation chromatography (GPC).

Poly[(methyl methacrylate)-co-(glycidyl methacrylate)] (PMMA(G)) was synthesized via free-radical polymerization using 0.5 wt-% of 2,2′-azoisobutyronitrile (AIBN) based on the monomer. The inhibitor was removed from commercial methyl methacrylate (MMA) by extraction with an aqueous 10 wt-% sodium hydroxide solution, while glycidyl methacrylate (GMA) was purified using vacuum distillation. Vacuum distillation of the GMA monomer is necessary to avoid any cross-linking of the polymer during the synthesis. Glass vials were filled with the monomer and initiator mixture and sealed under nitrogen atmosphere. The sealed vials were held in a thermostated bath at 60°C until a yield of approximately 10 wt.-% of the polymer was obtained. Toluene was then added to the polymer solution and the polymer was precipitated with methanol. The polymer was dissolved in toluene and precipitated in methanol once again for purification. The precipitate was isolated and dried in a vacuum oven. The PMMA(G) sample used in this study contains 1.4 mol-% of GMA as measured by NMR. The multifunctional agent 4,4′-methylenebis(o-chloroaniline) (MOCA) was used as a cross-linking agent for PMMA(G).

The film specimens of PS(OH)/PMMA(G) blends for optical microscopy observation were obtained as follows: homogeneous CHCl\(_3\) solutions containing 6 wt.-% polymer in total were first prepared, then the solvent was evaporated in a cover glass at about 30 °C, followed by a further drying at 60 °C under vacuum for more than 3 d. The films are about 30 μm thick.

The phase diagram of the PS(OH)/PMMA(G) mixture was described in some earlier papers\(^{11}\); here we only mention the parts relevant to the present study. The light scattering profile \(I(q)\) (relative scattered intensity \(I\) versus scattering vector \(q\)) under a Vv (parallel polarized) optical alignment was determined using a two-dimensional CCD-camera detector with 512 \(\times\) 512 pixels and an intensity resolution of 256 levels. The magnitude \(q\) of the scattering vector \(q\), corresponding to the wave number of concentration fluctuation, is defined by

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some of the samples. This behavior is indicated by the open circles in Fig. 1. After annealing at a temperature above 150°C for 24 h, some films became translucent and a phase-separated structure was observed under the microscope. This is indicated by the solid squares in Fig. 1. The single-phase nature of the blend was carefully confirmed by further annealing for 24 h. On the basis of these observations, the boundary line between one-phase and two-phase region (coexistence curve) is drawn somewhat arbitrarily in Fig. 1, thus a LCST phase diagram is attained. Fig. 1 also shows the glass transition temperature ($T_g$) curve, estimated by the Fox equation using $T_g$ data of pure PS(OH) and PMMA(G).

The LCST is expected to go down and the two-phase region to prevail in the phase diagram, when the molecular weight of PMMA(G) increases with its degree of cross-linking. Meanwhile, the $T_g$ of the mixture is elevated when the cross-linking reaction proceeds. Consequently, the blend located at the one-phase region initially becomes unstable when the two-phase region of the blend

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**Fig. 1.** Phase diagram of PS(OH)/PMMA(G) blends

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**Fig. 2.** Light scattering patterns photographed at various times following a phase separation during the cross-linking reaction of the 50/50/0.7 (w/w/w) PS(OH)/PMMA(G)/MOCA mixture at 170°C
reaches the experimental temperature and then undergoes a phase separation. The phase separation in the blends of 40/60 and 50/50 (w/w) PS(OH)/PMMA(G) loaded with MOCA was selected to be studied at different temperature.

A PS(OH)/PMMA(G) blend loaded with MOCA, e.g., PS(OH)/PMMA(G)/MOCA = 50/50/0.7 (w/w/w), is a single-phase system at the reaction temperature and no appreciable light scattering is detected from the mixture blend in the early stages of reaction. After a certain time lag, the light scattering pattern develops a characteristic azimuthally symmetric ring (the “spinodal ring”) which increases in intensity and decreases in scattering angle with time. This situation is demonstrated by a series of photographs taken at various times as shown in Fig. 2. The ring pattern implies the development of a regularly phase-separated structure. Also indicated is the lack of a preferred orientation of the structure in the plane parallel to the film surface. A typical optical micrograph of the specimen after reaction is given in Fig. 3, clearly showing a modulated structure with the morphological features of a unique periodicity and co-continuous phases. The modulated structure shown in Fig. 3 is quite similar to that by conventional isothermal spinodal decomposition. The morphologies obtained for other blends and temperatures show the same modulated-structure feature but the periodic distances of the structures vary with temperature and composition. The ring pattern and the modulated structure demonstrate that SD takes place during the cross-linking reaction of PMMA(G) for an initially single-phased PS(OH)/PMMA(G) blend.

Fig. 4 shows time-resolved light scattering profiles during SD induced by cross-linking at 170°C for the blends of 50/50/0.7 (w/w/w) PS(OH)/PMMA(G)/MOCA. The relative intensity levels of profiles taken at a give time can be compared within this figure, and the phase separation time progresses in the order of parts (b)–(a). With increasing time after a temperature jump from room temperature to 170°C, the scattering maximum appears after a time lag, indicating the onset of SD. This peak scattering vector \( q_m \) shifts toward smaller \( q \) and the peak intensity \( I_m \) increases, indicating that a coarsening of the structure proceeds to minimize its free energy by minimizing its interfacial area. The coarsening continues for a period of time and eventually the shift in \( q_m \) and the intensity increase in \( I_m \) stop at 1600 s, indicating that the coarsening of the phase-separated structure is pinned by the cross-linking. Scattering profiles obtained for other blends and temperature are qualitatively similar. However, various quantitative aspects of these data, such as the time dependence of \( q_m \), vary considerably with reaction temperature and compositions as discussed below.

**Dynamics of SD induced by a cross-linking reaction**

Fig. 5 and 6 show the time dependence of the peak scattering vector \( q_m(t) \) for blends of 50/50/0.7 and 40/60/0.8 (w/w/w) PS(OH)/PMMA(G)/MOCA at different temperatures. The time-evolution behavior of the scattered light intensity during phase separation is not considered here because of the inaccuracy due to succeeding varia-

![Fig. 3. Typical optical micrograph showing the modulated structure yielded by spinodal decomposition induced by a cross-linking reaction; PS(OH)/PMMA(G)/MOCA = 50/50/0.7 (w/w/w), reaction temperature = 130°C.](image3)

![Fig. 4. Time-resolved light scattering profiles during spinodal decomposition induced by the cross-linking reaction of the 50/50/0.7 (w/w/w) PS(OH)/PMMA(G)/MOCA mixture at 170°C.](image4)
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Fig. 5. Time dependence of the peak scattering vector $q_m(t)$ during spinodal decomposition at various reaction temperatures for the 50/50/0.7 (w/w/w) PS(OH)/PMMA(G)/MOCA mixture.

Fig. 6. Time dependence of the peak scattering vector $q_m(t)$ during spinodal decomposition at various reaction temperatures for the 40/60/0.8 (w/w/w) PS(OH)/PMMA(G)/MOCA mixture.

ation of the refractive index of the PMMA(G) component with continuing cross-linking reaction. As seen from Fig. 5 and 6, in the earlier time region (referred to as region I hereafter), $q_m(t)$ decreases rapidly but in the succeeding region (region II), the rate of decrease of $q_m(t)$ slows down gradually. Eventually, $q_m(t)$ is found to be effectively pinned on time scales longer than a composition-dependent pinning time $t_p$ (region III). $q_m(t)$ in region I can be expressed approximately by a scaling relation

$$q_m(t) \propto t^{-\alpha}$$

(2)
similar to that observed for the spinodal decomposition in the absence of a reaction\textsuperscript{12}. However, in region II the time evolution of $q_m(t)$ deviates from this scaling relation and the simple scaling relation as given in Eq. (2) is not valid in this region (the exponent $\alpha$ is time dependent and tends to decrease toward zero at $t > t_p$), reflecting that the coarsening process is retarded by the cross-linking reaction. The rate of phase separation depends on the product of mobility and thermodynamic driving force\textsuperscript{13}. The thermodynamic driving force is proportional to the quench depth defined by $|T - T_s|$, where $T$ and $T_s$ are the temperature of phase separation (reaction temperature) and spinodal point, respectively. For the phase separation in the present system, $T_s$ decreases with the reaction resulting in a succeeding increase of the quench depth. On the contrary, the mobility decreases with continuing reaction. The contribution of the latter to the phase separation rate may be dominant over the contribution of the former. Therefore the phase separation is slowed down with increasing reaction (in region II).

The values of $\alpha$ (in region I), the pinning time $t_p$, and the wave number for the pinned structure $q_{mp}$ for different temperatures and blends are summarized in Tab. 1. It is found that the values of $\alpha$, $t_p$, and $q_{mp}$ all depend on the temperature, i.e. the higher the temperature is, the larger is $\alpha$, the shorter is the time for pinning $t_p$ and the smaller is the characteristic wave number $q_{mp}$ for the pinned structure (hence the larger is the periodic distance $A_{mp}$ of the pinned structure ($A_{mp} = 2\pi/q_{mp}$)).

The results shown in Tab. 1 may be qualitatively interpreted in terms of the relative rate of spinodal decomposition compared to that of cross-linking reaction. It should be noted that the rate of spinodal decomposition and cross-linking reaction are both dependent on time; for simplicity, here we discuss the mean rate before vitrification or gelation. When the reaction is carried out at a temperature close to the coexistence curve, the reaction rate should be high, causing the LCST curve to go down fast. Consequently, the phase separation proceeds usually under a larger thermodynamic driving force. Furthermore, the mobility of the components should be relative large at high temperatures. Thus the phase separation rate is also high (larger $\alpha$ value). However, the phase separation (coarsening process) may proceed much faster than the reaction, thereby the phase structure can grow sufficiently to give morphologies with longer periodic distances (small $q_{mp}$).

When the reaction occurs at a temperature near $T_g$, both the rate of the cross-linking reaction and the rate of the phase separation should be small. The small rate of phase separation (small $\alpha$ value) may be referred to the

<table>
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<tr>
<th>PS(OH)/PMMA(G) (w/w)</th>
<th>Temperature $^\circ$C</th>
<th>$t_p \times 10^{-3}$ s</th>
<th>$q_{mp}$ $\mu$m$^{-1}$</th>
<th>$\alpha$</th>
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<tr>
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<td>234.3</td>
<td>3.28</td>
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<td>16</td>
<td>1.5</td>
<td>0.64</td>
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<tr>
<td>170</td>
<td>1.6</td>
<td>0.55</td>
<td>1.18</td>
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</tr>
<tr>
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<tr>
<td>170</td>
<td>0.6</td>
<td>1.32</td>
<td>0.66</td>
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</table>

Table 1. Pinning time $t_p$, characteristic wave number $q_{mp}$ at which the pinning occurs and power value $\alpha$ of the time evolution of $q_m$ for the spinodal decomposition during cross-linking reaction.
relative low mobility and small thermodynamic driving force. However, the reaction may proceed slightly faster than the phase separation, thereby the phase structure fails to grow sufficiently, resulting in morphologies with shorter periodic distances (larger $q_{np}$).

Fig. 5 and 6 also show that the time evolution of $q_{m}(t)$ is composition-dependent. By comparing the phase separation at the same temperature for the two compositions 50/50 and 40/60 (w/w) PS(OH)/PMMA(G), it is found that $a$ and $t_p$ become smaller, and $q_{np}$ becomes larger when the content of PMMA(G) increases from 50 to 60 wt.-% of the blend. These results may be referred to the increase of $T_g$ of the blends, i.e. $T_g$ in the 40/60 blend is higher than in the 50/50 blend according to the Fox equation, resulting in a relative low mobility for the 40/60 blend compared with that for the 50/50 blend at the same temperature. Thus the phase separation proceeds relative slowly (small $a$ value) for the 40/60 blend. Furthermore, it is prevented by the cross-linking in an earlier stage (small $t_p$) for the 40/60 blend than for the 50/50 blend. In other words, the cross-linking reaction influences the phase separation more effectively for the 40/60 blend than for the 50/50 blend due to the relative small gap between the reaction temperature and $T_g$ for the 40/60 blend compared with the gap for the 50/50 blend.

As discussed above, in the present phase-separation experiments, there exists a competition between the reaction and the phase separation. The phase separation is activated by the cross-linking reaction, but the reaction tends to inhibit the polymer diffusion via the network formation, hence the coarsening process of the phase-separated structure is retarded and arrested by the reaction. It can be found that, based on the above results, the former effect is remarkable at temperatures close to the coexistence curve, whereas the latter effect is dominant for the cross-linking reactions carried out in the vicinity of $T_g$ of the blends.

Thus, the phase-separation process is found to be dramatically affected by the chemical reaction during spinodal decomposition. Presently, an intriguing problem is whether the relation of the chemical reaction with the phase separation can be described with a simple scaling relation. Based on computer simulations of a binary mixture simultaneously undergoing a spinodal decomposition and a chemical reaction $A \leftrightarrow B$, a scaling relation has been proposed for the time evolution of the phase structure in this case$^{13}$, i.e.

$$q_{m}(t) \propto t^{-a} \cdot f(x)$$  \hspace{1cm} (3)

where

$$s = k \cdot t$$

Here $k$ and $t$ are the reaction rate and reaction time, respectively. $f(x)$ is a function accounting for the behavior of the interplay of chemical reaction with phase separation. $a$ is the same exponent characterizing the growth of the structure as in Eq. (2).

In Fig. 7 and 8, $q_{m}(t) \cdot t^a$ is plotted double-logarithmically versus time $t$ for 50/50 and 40/60 PS(OH)/PMMA(G) blends, respectively. We find that the data satisfy the scaling relation shown in Eq. (3). We further note that the asymptotic behavior of the function $f(x)$ in the two extreme time regions can be summarized as

$$f(x) = \text{const.} \quad \text{for } t \ll \infty$$

and

$$f(x) \propto t^\nu \quad \text{for } t \rightarrow \infty$$  \hspace{1cm} (4)

This is consistent with the results given by computer simulations$^{13}$.

Our experimental results thus support the scaling relation of Eq. (3) describing the behavior of phase separation under the influence of a chemical reaction. However, it should be noted that there are still some open questions in
the dynamics of spinodal decomposition induced by a reaction, e.g. the asymptotic behavior of the function $f(x)$ in the intermediate time stage (region II), and the temperature and composition dependence of the $\alpha$ values and the wave number $q_{wmp}$ for a pinned domain structure. Therefore, further experimental and theoretical studies on this subject are necessary for elucidating the behavior of the interplay between a chemical reaction and the phase separation.

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