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Viscoelastic Phase Separation Induced by Polymerization of *n*-Butyl Methacrylate in the Presence of Poly(dimethylsiloxane-*co*-diphenylsiloxane)

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ABSTRACT: Morphological development of phase-separated domains was observed in polymerizing *n*-butyl methacrylate system by using a phase contrast microscope. Three distinct structures, namely, droplets, network, and spongelike domains, formed in the order of increasing initial monomer weight fraction *w*. The network and spongelike structure closely resembled those observed in the viscoelastic phase separation of a nonreacting system, but droplets formed at lower *w* showed rather characteristics of the normal phase separation: The droplets coalesced easily by collisions and had a wide size distribution. In addition to the crossover behavior from the viscoelastic to the normal phase separation with decreasing *w*, it was also observed that phase separation dynamics at a fixed *w* changed from the normal to the viscoelastic with a lapse of phase separation time. Comparison with the 4-cholostyrene/poly(dimethylsiloxane-*co*-diphenylsiloxane) (PDMSDPS) system, in which noncoalescing droplets with narrow size distribution (the moving droplets) formed over a wide range of *w*, was made, and the origins of the difference in the morphological development between these systems were discussed. It was speculated that the segregation strength between PDMSDPS and polymerization product was a primary cause of the difference in morphological structures.

Introduction

In polymerization reaction induced phase separation, interesting patterns that normally cannot be observed in a nonreacting system may occur because of the interplay between chemical reaction and phase separation.[1−10] Recently it was found that a crystal-like array of droplets formed in a polymerizing phase separation system induced by radical polymerization of 4-chlorostyrene monomer in the presence of random copolymer of dimethylsiloxane and diphenylsiloxane (PDMSDPS).[11,12] In an early stage of phase separation, the phase being rich in the reaction product, poly(4-chlorostyrene) (P4CLS), formed spherical domains with quite narrow distribution in size. These droplets were moving about incessantly and collided with each other, but they hardly coalesced. With the proceeding of the reaction, the droplets were growing in size without broadening their size distribution and eventually arranged themselves in crystal-like arrays. It was considered that this spontaneous formation of an ordered array was caused by the mechanism similar to the one for the Alder transition of hard spheres with uniform size, since the P4CLS-rich droplets showed a close resemblance to hard spheres in that they did not either coalesce by collisions or had an attractive interaction strong enough to cohere with each other.

Noncoalescing droplets with narrow size distribution have already been observed in phase separation of a nonreacting mixture.[13,14] When a mixture of components having largely different viscoelastic properties is quenched deeply into the two-phase region at an off-critical composition, such noncoalescing droplets form. This is one of the distinctive features of the phenomenon known by the name of "viscoelastic phase separation".[15] Since PDMSDPS was fluid at ambient temperature and had much lower molecular weight ($\mathrm{MW} = 2200$) than P4CLS (typical $\mathrm{MW} \sim 5 \times 10^5$), it was conceived that noncoalescence and narrow size distribution of droplets resulted from a large difference in viscoelastic properties between P4CLS and PDMSDPS. Since no array formed in viscoelastic phase separation of a nonreacting system, the unusual array structure was distinctive of the viscoelastic phase separation induced by polymerization reaction.

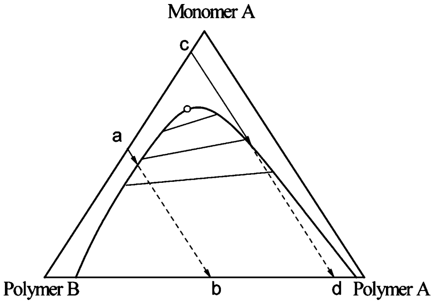

Figure 1. Schematic ternary phase diagram of a system undergoing phase separation induced by radical polymerizaton of monomer A in the presence of polymer B.

In a radical polymerization, by which P4CLS was produced, the molecular weight of the product polymer does not change, and the number of polymer molecules increases with reaction conversion. Thus, the process of phase separation induced by radical polymerization is described with using a ternary phase diagram schematically illustrated in Figure 1. As polymerization reaction proceeds, the composition of a mixture changes along a straight line parallel to the side connecting the vertexes of the monomer A and its product polymer A. Phase separation is caused by segregation between two different polymer species

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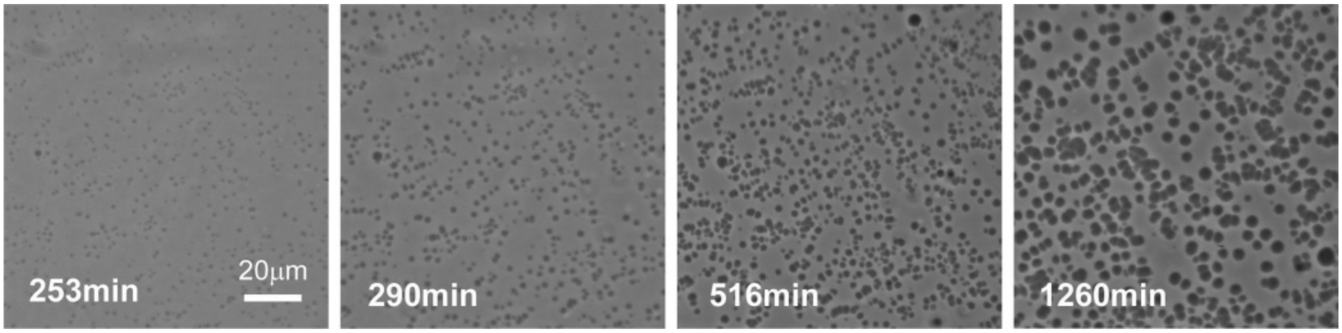

Figure 2. Phase contrast optical micrographs of morphological development for sample BMA/PDMSDPS with initial monomer weight fraction $w = 0.50$ at $T = 100$ °C. The reaction and phase separation time is indicated in the figure.

A and B, and thus the phase boundary has a shape as shown in Figure 1. In the case of nonreacting binary mixture with viscoelastic asymmetry, the viscoelastic phase separation occurs by a deep quench, and three distinctive morphologies, namely, moving droplets, networks, and spongelike domains, form depending on the composition of higher viscoelastic component.[13−16] Similar behavior is expected for a nonreacting ternary mixture of polymer−polymer−solvent if viscoelastic asymmetry exists between these two polymers. In a polymerization-induced phase separation viscoelastic asymmetry is also expected to play an important role; however, the local composition is changed by both phase separation and polymerization reaction, which makes the morphological development of phase-separated domains different from those in phase separation of a nonreacting mixture.[7,17−19] Therefore, no simple correspondence is expected between viscoelastic phase separation with and without polymerization reaction involved. In fact, in the 4CLS/PDMSDPS system, neither network nor spongelike domain was observed in our investigated composition range from 0.20 to 0.70 (weight fraction of the monomer), although the total volume of the droplet phase became sufficiently large at high reaction conversions. On the other hand, in the polymer-dispersed liquid crystal, a network or spongelike structure formed in general,[20−23] which was considered to form by polymerization-induced viscoelastic phase separation.[15]

The present understanding of the mechanisms of the crystal-like array formation still remains at a primitive stage. This is mainly due to the fact that dynamics of polymerization-induced viscoelastic phase separation is not well studied and poorly understood. In the present work, we further explored phase separation dynamics by using *n*-butyl methacrylate as monomer with the same nonreacting component in order to gain an insight into the mechanisms of polymerization-induced viscoelastic phase separation.

Experimental Section

The monomer *n*-butyl methacrylate (BMA), which was purchased from Beijing Xin Guang Chemical Reagent Co., was washed with 10% sodium hydroxide aqueous solution to remove an inhibitor and dried over calcium chloride, followed by distillation under reduced pressure. Purified monomer was stored in a closely sealed container, which was kept in a refrigerator until use. Random copolymer of dimethylsiloxane and diphenylsiloxane with a diphenylsiloxane content of 29 mol % was used, which was the same sample as used in a previous work. It was a product of Shin-Etsu Chemical Co. (Product name KF54) and had the number-average molecular weight $M_n = 2.2 \times 10^3$ and the approximate molecular weight distribution index $M_w/M_n = 2.0$. The details of characterization method for the copolymer were given in the previous paper.[12] The initiator benzoyl peroxide (BPO) was a product of Beijing Reagent Co. and was purified by the conventional recrystallization method from an ethanol solution.

After benzoyl peroxide was dissolved in *n*-butyl methacrylate, the solution was stirred for 30 min. Then it was mixed with poly(dimethylsiloxane-*co*-diphenylsiloxane) (PDMSDPS) and was further stirred for 2 h at room temperature to ensure complete mixing. The initiator fraction θ was fixed at 1.0×10^{-4} of the total weight of a mixture in the present experiments. The sample mixture was sandwiched between a round slide glass of 16 mm in diameter and a cover glass with poly(tetrafluoroethylene) spacer of 0.05 mm thickness, and then it was placed in a brass holder of 35 mm in diameter and 4 mm thick. The holder had two windows for observation of the phase-separated domains. Polymerization and phase separation were made on a hot stage Linkam LTS350. Evolution of phase-separated domain structure was observed at 100 °C with a phase-contrast microscope. Microscopic image taken by a video camera was recorded on videotape continuously in an initial period and intermittently in a later period.

The reaction conversion of BMA was determined by ^{1}H NMR (Bruker AV400). Since a relatively large amount of sample was required to obtain a reliable value, a glass tube was used as a reaction vessel in determination of conversion instead of the combination of slide and cover glasses used in microscope observation. The reacted mixture was dissolved in deuterated chloroform. The difference in the chemical shift of two protons of the $-OCH_2-$ group between a BMA monomer (4.146 ppm) and poly(*n*-butyl methacrylate) (3.935 ppm) was used for evaluating the existing ratio of these two molecular species. The accuracy of the method was checked by evaluating the ratio of a test mixture with known composition, and a reasonable agreement was obtained.

The relative molecular weight $(M_w)_r$ of poly(*n*-butyl methacrylate) (PBMA) produced by polymerization reaction was measured with a size-exclusion chromatograph apparatus Waters 515 HPLC pump/2410 refractive index detector/Styragel columns HT3, HT5, and HT6E at 30 °C.

A ratio of the volume of PBMA-rich phase to the total volume of a demixed sample was evaluated from an optical micrograph by digital image analysis. The original 256-grayscale image of domains was converted into a black-and-white image by using the software Scion Image Beta 4.02, and then the area of PBMA-rich phase was evaluated by using the software Origin 7.0.

Results and Discussion

Development of phase-separated domain structures that was observed at 100 °C for several initial monomer weight fractions *w* with using a phase contrast microscope is shown in Figures 2−5.[29]

In the case of $w = 0.50$, small spherical domains appeared at $t = 219$ min. Each domain grew in size, but its location was fixed in space, indicating that it was a hole formed in a matrix phase of higher viscoelasticity. The holes increased in number and grew in size with time, leading to the formation of a spongelike structure, as shown in Figure 2.

In the case of $w = 0.30$ (shown in Figure 3), holes similar to those observed for $w = 0.50$ appeared at $t = 109$ min and grew more rapidly than in the case of $w = 0.50$. With the growth of

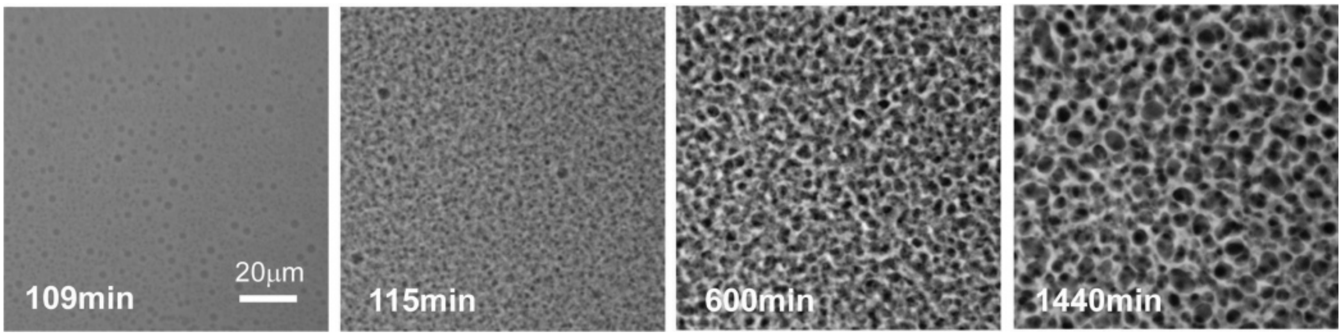

Figure 3. Morphological development for sample $w = 0.30$ (at $T = 100$ °C).

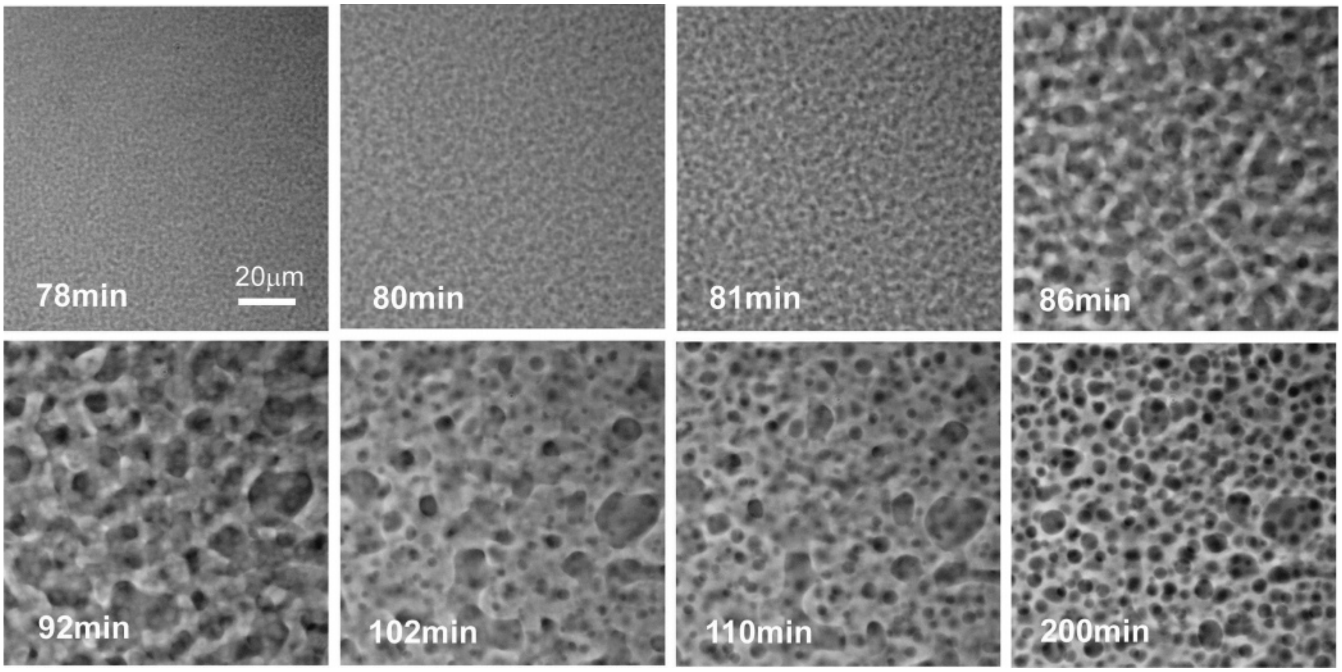

Figure 4. Morphological development for sample $w = 0.15$ at $T = 100$ °C.

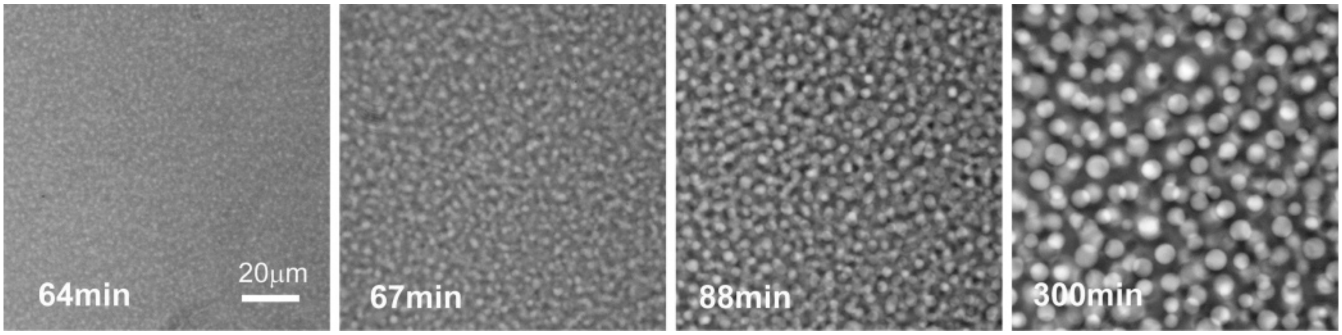

Figure 5. Morphological development for sample $w = 0.10$ at $T = 100$ °C.

holes, the continuous domain became thinner and the spongelike domain was turned into a network. The links of the network were elongated, and some of them were broken with the further growth of holes, but the phase inversion did not occur within our observed period of 72 h. Formation of the network structure was a characteristic of the viscoelastic phase separation in a nonreacting system, and the present result showed that the similar morphological structure formed in the polymerization-induced phase separation as well when there was a large difference in viscoelasticity between two segregating phases. Since PBMA has a higher viscoelasticity, the network must correspond to the PBMA-rich phase. Similar networks were observed at $w = 0.20$ and 0.40. Holes appeared earlier as w decreased: $t = 150$ min at $w = 0.40$ and $t = 84$ min at $w = 0.20$. The growth rate of holes increased with the decreasing w: The average mesh size of the network at high monomer conversion ($t = 12$ h) was 1−2 μm for $w = 0.40$ and about 10 μm for $w = 0.20$.

In the case of $w = 0.15$, bicontinuous domains similar to those observed in spinodal decomposition of a nonreacting and dynamically symmetric mixture formed initially ($t = 78$ min), as seen in Figure 4, instead of holes observed in an early stage of phase separation for higher initial monomer compositions. The bicontinuous domains coarsened rapidly, and the PBMA-rich domain gradually changed into a network. Small holes appeared in the links of the network around $t = 100$ min, and

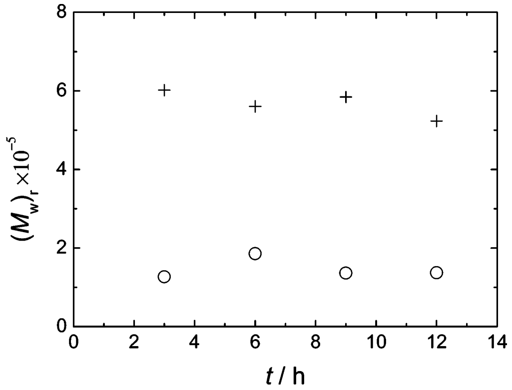

Figure 6. Relative molecular weights $(M_w)_r$ of poly(n-butyl methacrylate) and poly(4-chlorostyrene) polymerized at $w = 0.50$ and $T = 100$ °C for a period of t: PBMA (○) and P4CLS (+).

those holes grew faster than voids surrounded by the network links. Eventually holes and voids (they differed in size but corresponded to the same PDMSDPS-rich phase) became indistinguishable, resulting in formation of a network with a finer average mesh size.

When the initial monomer fraction was decreased further to $w = 0.10$, PBMA-rich droplets formed by phase separation, as shown in Figure 5. These droplets had rather wide distribution of size and coalesced easily by collisions, which made a marked contrast with the moving droplets observed in the 4-chlorostyrene system. Further observation was made at $w = 0.12$, 0.07, and 0.05, but morphological development of phase-separated domains was similar to the one at $w = 0.10$, and noncoalescing droplets with narrow size distribution were not observed.

In the present system, three distinctive morphologies, droplets, network, and spongelike structure, similar to those observed in the viscoelastic phase separation of the nonreacting system, formed in the order of increasing initial monomer composition. However, the correspondence between the present system and the viscoelastic phase separation of nonreacting system was only partial because droplets formed at lower w displayed characteristics of the normal phase separation. In other words, the present system showed a crossover behavior from the viscoelastic to the normal phase separation with decreasing initial monomer composition. In addition to the crossover with varying w, the crossover with proceeding of the polymerization reaction was also observed at a fixed initial monomer composition $w = 0.15$ seen in Figure 4. Initially, bicontinuous domains typical of the normal spinodal decomposition formed, while holes resembling those appearing at $w = 0.50$ (Figure 2) formed in the network links. These made a marked contrast with the 4CLS system. In the 4CLS system the moving droplets formed over a wide range of w, and coalescing droplets formed at higher w instead of network or spongelike domains.

Relative molecular weights $(M_w)_r$, which were determined by size-exclusion chromatography, of poly(n-butyl methacrylate) polymerized at $w = 0.50$ and $T = 100$ °C for a period of t are shown in Figure 6, together with the molecular weights of poly(4-chlorostyrene) polymerized under the same conditions. The molecular weight of PBMA did not change with the reaction time (conversion) as was well-known for a product of radical polymerization. The average relative molecular weight of PBMA (1.3×10^5) was roughly one-fourth of that of P4CLS. The difference was probably caused by the amount of the initiator used in the reaction: No initiator was used in polymerization of P4CLS.

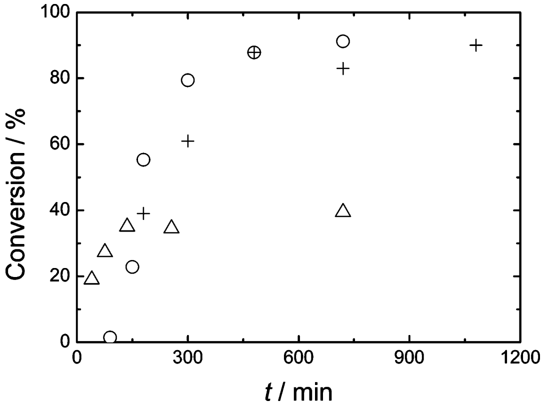

Figure 7. Reaction conversion of BMA in a mixture with PDMADPS at $w = 0.50$ (○), $w = 0.15$ (△), and 4CLS at $w = 0.50$ (+). Reaction temperature was 100 °C.

The temporal change of the reaction conversion of BMA at $w = 0.50$ and 0.15 ($T = 100$ °C) is shown in Figure 7, together with the result of 4CLS ($w = 0.50$). Reaction proceeded rapidly at the beginning and gradually decelerated with consumption of monomers. The final conversion at $w = 0.15$ was quite low (about 40%), but the weight fraction of unreacted monomer remaining in the mixture was 9% and was not so much different from the value 6% at $w = 0.50$. Compared at $w = 0.50$, BMA reacted slightly faster than 4CLS, but the difference was not large.

Several factors were conceivable as the origins of the observed difference in morphological development between the BMA and the 4CLS systems. There was a large difference in the glass transition temperature T_g between PBMA ($T_g = 293$ K) and P4CLS ($T_g = 388-401$ K).[24] In addition, PBMA had lower relative molecular weight than P4CLS, as seen in Figure 6. Thus, it was considered that there was a higher asymmetry of viscoelasticity between two separated phases in the 4CLS system.[25] This probably explained that in the 4CLS system viscoelastic phase separation (moving droplets) was observed over a wide range of w including low w while in the BMA system normal phase separation was observed at lower w. However, the difference in viscoelastic asymmetry cannot explain why network did not form at higher w in the 4CLS system.

It is well-known that the morphological structure of phase-separated domains depends on the relative volumes of the coexistence phases in a nonreacting system.[26−28] This also applies to the phase separation induced by polymerization reaction, but the dependence is much more complicated because the relative volumes of coexistence phases change with the reaction conversion. In addition, the morphological development in polymerization-induced phase separation depends on the relative rate between the reaction and phase separation as well as the coexistence phase volume at each moment.[17,18] Therefore, different morphological structure will form depending on the reaction rate, even when the reaction proceeds along the same path in phase diagram.

At $w = 0.50$ the overall reaction rate of BMA was slightly faster than that of 4CLS, as seen in Figure 7. In the case that the reaction proceeds along the path ab drawn in Figure 1, droplets of polymer A-rich phase will form initially if reaction is slow compared with the phase separation since phase separation proceeds in the vicinity of the phase boundary, while network or spongelike structure is more likely to form initially if reaction is sufficiently fast. Thus, the experimental results of reaction rates seemed qualitatively compatible with observed difference in morphological development between these two systems. However, the difference in reaction rate was not large,

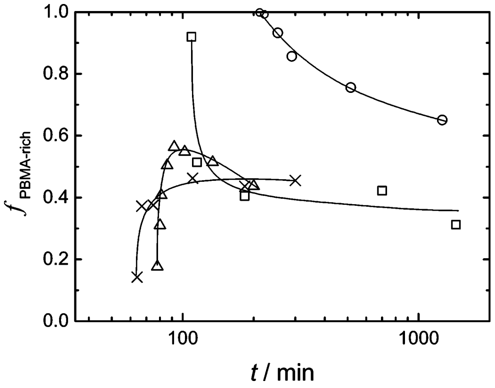

Figure 8. Temporal change of a fraction of the volume of PBMA-rich phase at different initial monomer weight fraction: $w = 0.50$ (○), 0.30 (□), 0.15 (△), and 0.10 (×). The lines in the figure are used only to guide the eye.

and it was unlikely that the relative reaction rate alone accounted for the difference. Furthermore, at lower w, behavior characteristic of the normal phase separation, which was expected in a shallow quench region, was observed in the BMA system rather than in the 4CLS system: PBMA-rich droplets formed at $w = 0.10$ coalesced by collisions, and bicontinuous structure typical of normal spinodal decomposition formed initially at $w = 0.15$. Thus, the reaction rate could not consistently explain the difference in morphological development between the BMA and 4CLS systems.

Though the reaction path alone cannot determine morphological development in polymerization-induced phase separation as mentioned above, we can distinguish at least two classes of the reaction paths by their intersecting points with the coexistence curve. When the system is destabilized on the polymerization product-poor side of the coexistence curve (ab in Figure 1), the product polymer-rich phase becomes a miner phase and increases its volume with the proceeding of the reaction, and when it was destabilized on the other side (cd in Figure 1), the product polymer-rich phase becomes a major phase and decreases its volume. Morphological development will be quite different between these two cases, whether reaction is faster than phase separation or not.

In Figure 8, the temporal change of a fraction of the volume of PBMA-rich phase, $f_{\text{PBMA-rich}}$, evaluated by the image analysis of optical micrographs for four initial monomer compositions. At two low compositions $w = 0.10$ and 0.15, initially $f_{\text{PBMA-rich}}$ increased rapidly with time, while at higher compositions $w = 0.30$ and 0.50, it decreased. The results indicated that the reaction path intersects with the PBMA-poor branch of phase diagram at two lower compositions and intersects with the PBMA-rich branch at two higher compositions. At $w = 0.15$, $f_{\text{PBMA-rich}}$ initially increased with the reaction conversion and then began to decrease after it passed a maximum. In viscoelastic phase separation, the phase volume fraction of a higher viscoelastic phase is known to decrease with time.[15] At this composition the crossover from the normal to the viscoelastic phase separation was observed, and thus the decrease in $f_{\text{PBMA-rich}}$ in the later period could be explained by the viscoelastic effect. The phase volume fractions at a sufficiently long time were not on the order of w, which was unreasonable. Probably it was caused by the errors in projecting a 3-dimensional structure to a 2-dimensional image. Though the absolute value was not so reliable, Figure 8 was considered to represent the trends of time dependence of $f_{\text{PBMA-rich}}$ at each w correctly.

Geometrical consideration shows that when the two-phase region becomes broad, most reaction path intersect with a coexistence curve on the product-polymer-poor side. So, the results shown in Figure 8 suggested that BMA system had narrower two-phase region, in other words, that it showed weaker segregation than 4CLS systems. The minimum amount of methanol, which was a poor solvent for PDMSDPS, necessary to demix 50 wt % BMA/PDMSDPS mixture was found to be 3 times as much as the amount necessary to demix the 50 wt % 4CLS/PDMSDPS mixture at room temperature. The result was reasonably compatible with our speculation for the difference in the segregation strength between the two systems, although it did not justify our speculation since the interaction between monomer and methanol was neglected here, and the difference between monomer and polymer should be taken into account in the proper discussion.

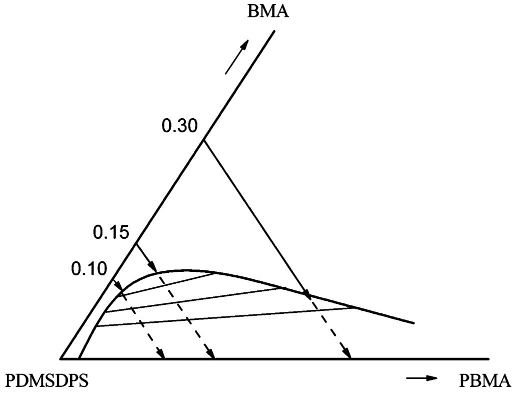

Figure 9. Schematic phase diagram of polymerization induced phase separation in the BMA/PDMSDPS system.

From the above discussion, we considered that difference in segregation strength was the primary cause for the difference in observed morphological structures between the BMA system and the 4CLS system. We speculated the mechanism of morphological change as follows.

A speculated rough sketch of the phase diagram of the BMA/PBMA/PDMSDPS system is shown in Figure 9. The two-phase region was relatively narrow, reflecting the weak segregation between PBMA and PDMSDPS, and the phase diagram was highly asymmetric because of the large difference in chain length between PBMA and PDMSDPS.

In the case of $w = 0.10$, the reaction path intersected with the coexistence curve on the PBMA-poor side. The reaction proceeded rapidly at the beginning but gradually decelerated as monomer was consumed. The reaction rate already became slow when the system got into the two-phase region, and phase separation proceeded in the shallow region relatively close to the phase boundary. Consequently, normal phase separation behavior at an off-critical composition would be observed. Droplets thus formed were growing in size by absorbing BMA monomers and PBMA produced by polymerization reaction and also by coalescence.

In the case of $w = 0.15$, the reaction path intersected with the coexistence curve at a point close to the critical point. Like as in the case of $w = 0.10$, the reaction rate had already become slow compared with phase separation when the system got into the two-phase region. Normal phase separation occurred to form bicontinuous domains typical of those observed in the critical concentration range. With proceeding of the reaction and phase separation, PBMA concentration and thus its viscoelasticity increased in the PBMA-rich phase. Eventually viscoelastic asymmetry began to control the phase separation dynamics in the PBMA-rich continuous domains, and holes formed in the PBMA-rich phase. The change in phase separation dynamics from the normal to the viscoelastic one was reflected in the decrease of the volume of PBMA-rich phase. In the case of $w = 0.30$, the mixture was destabilized on the PBMA-rich side of the coexistence curve, and the PDMSDPS-rich phase formed droplets or holes in the PBMA-rich matrix. The total volume of the PDMSDPS-rich phase increased with proceeding of the reaction and eventually droplets connected with each other, turning the PBMA-rich matrix phase into a network. In the case of $w = 0.50$, similar to the case of $w = 0.30$, the mixture was destabilized on the PBMA-rich side of the coexistence curve, and the PDMSDPS-rich phase formed droplets. With proceeding of reaction and phase separation, droplets grow, but the coalescence of droplets did not take place so much as to form a network, since the final phase-volume fraction of the PBMA-rich phase was relatively large.

Conclusion

In liquid−liquid phase separation induced by radical polymerization of *n*-butyl methacrylate in the presence of random copolymer poly(dimethylsiloxane-*co*-diphenylsiloxane), three distinct phase-separated domain structures, namely, droplets, network, and spongelike domains, were observed with increasing initial monomer concentration. Poly(*n*-butyl methacrylate) produced by the reaction had much longer chain length than the copolymer PDMSDPS, and consequently the large viscoelastic asymmetry existed between two demixing phases. In the viscoelastic phase separation of a nonreacting binary mixture, similar morphological structures were known to form depending on the composition. The network and spongelike domains formed in the present system closely resembled those observed in the viscoelastic phase separation of a nonreacting binary mixture. However, droplets observed at lower initial monomer compositions coalesced easily by collisions and their size distribution was wide, rather displaying characteristics of the normal phase separation. In addition to the crossover behavior from the viscoelastic phase separation to the normal phase separation with decreasing w, at $w = 0.15$ phase separation dynamic also changed from normal to viscoelastic in the phase separation process. The change in phase separation dynamics caused the formation of an unusual network structure consisting of porous links and could be useful in obtaining novel morphological structures.

The observed morphological developments made a marked contrast with those of the polymerization-induced phase separation of mixtures of 4-chlorostyrene with the PDMSDPS. In the latter system, noncoalescing droplets with narrow size distribution formed over a wide range of w, and either network or spongelike domains were not observed. It was speculated that the difference in morphological development between these two systems was primarily caused by the difference in the segregation strength. This was supported by a rough estimation of the relative compatibility of BMA and 4CLS with PDMSDPS. Although it is known that the relative rate between the reaction and phase separation in general played a significantly important role in morphological development of polymerization-induced phase separation, the relative rate could not be a main cause in this case because the reaction rate of BMA was not much different from that of 4CLS. It was explained that the three morphological structures formed depending on the location of intersection between the reaction path and the coexistence curve: Droplets formed when the reaction path intersected with the coexistence curve on the PBMA-poor side, network formed when the path intersected near the critical point, and spongelike domains formed when the path intersected on the PBMA-rich side.

According to the present interpretation of the results, moving droplets and thus crystal-like array of droplets could be produced in a strongly segregating system. Therefore, moving droplets, network, and spongelike domains were expected to be observed in a single system, as in the viscoelastic phase separation of nonreacting binary mixture, if this system had an appropriate segregation strength intermediate between the BMA and 4CLS systems.

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