Macromolecules **2005,** *38,* 7127−7133

Crystal-like Array Formation in Phase Separation Induced by Radical Polymerization

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Received April 27, 2005

ABSTRACT: A unique domain structure was found in liquid−liquid phase separation induced by radical polymerization of 4-chlorostyrene monomer in the presence of random copolymer poly(dimethylsiloxane-*co*-diphenylsiloxane). Over a wide range of temperature and initial monomer composition, poly(4-chlorostyrene)-rich droplets with narrow size distribution were generated by phase separation, and these droplets hardly coalesced by collisions. With the growth of droplet size, droplets gradually filled the space and spontaneously arranged themselves into a regular array like crystal. The threshold temperature, below which the array formed, decreased with increasing initial monomer composition. Poly(4-chlorostyrene) had much longer chain length and higher glass-transition temperature than the copolymer component, and noncoalescence of fluid droplets was explained by this asymmetry of viscoelasticity between the segregating components. The regular array was considered to form by a mechanism analogous to the Alder-type fluid-to-solid transition of hard spheres. A possible mechanism of this regular pattern formation was proposed.

Introduction

Because of the small entropy of mixing, most polymers are not compatible with other polymer species even when their monomers are compatible with each other. Consequently, an initially homogeneous mixture of a polymer and a monomer of different species is generally not stable with the polymerizing of the monomer, which induced phase separation. The phase separation induced by polymerization reaction is quite common in industrial processes. Since microscopic structures formed by phase separation could have significant effects on the performance of the product material, the dynamics of polymerization-induced phase separation (PIPS) has been studied extensively to control the domain structure.[1−11] In addition to its industrial importance, PIPS is an important subject of nonequilibrium statistical mechanics, and especially various patterns could result from the interplay between chemical reaction and phase separation; therefore, this subject has attracted considerable attention. Marked examples of patterns formed in phase separation induced by polymerization reaction or cross-linking reaction are the concentric pattern appearing in phase separation induced by photo-cross-linking of random copolymer poly(styrene-*co*-chloromethylstyrene) in the presence of poly(vinyl methyl ether)[12] and the salami pattern appearing in high-impact polystyrene.[13,14] The salami pattern was also observed recently in radical polymerization of 2-chlorostyrene in the presence of polystyrene.[15] Simulation studies of these interesting pattern formations have been also attempted to elucidate their mechanisms.[16,17]

In a preliminary work, we found a unique structure forming during phase separation induced by radical polymerization of 4-chlorostyrene monomer in the presence of random copolymer poly(dimethylsiloxane-*co*-diphenylsiloxane).[18] The pattern exhibited high regularity and symmetry, which made a striking contrast to previously known nonsymmetrical patterns formed during polymerization-induced phase separation. Although the highly regular pattern is commonly observed in microphase separation of block copolymer, such regularity was quite unexpected for liquid−liquid phase separation of a mixture containing no block copolymer. A noticeable difference between the present system and the other systems used in PIPS lies in the low viscosity of the nonreacting polymer component, which has high mobility at room temperature. This has been considered to play an essential role in the formation of symmetrical pattern. In the early preliminary report, experiments were carried out at a single composition and temperature, and the observation of morphological structure was mainly made for samples quenched to room temperature. In this work, we carried out experiments at various temperatures and compositions and made continuous observation in situ to acquire more detailed understanding of this unique phenomenon.

Experimental Section

The monomer 4-chlorostyrene (4CLS) was a product of Fluka Chemical Co. and was purified by distillation under reduced pressure after it was washed with 10% sodium hydroxide aqueous solution to remove an inhibitor and dried over calcium chloride. Purified monomer was stored in a refrigerator until use. A mixture of divinylbenzene isomers, which was used only in a supplementary experiment, was a

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10.1021/ma050896y CCC: $30.25

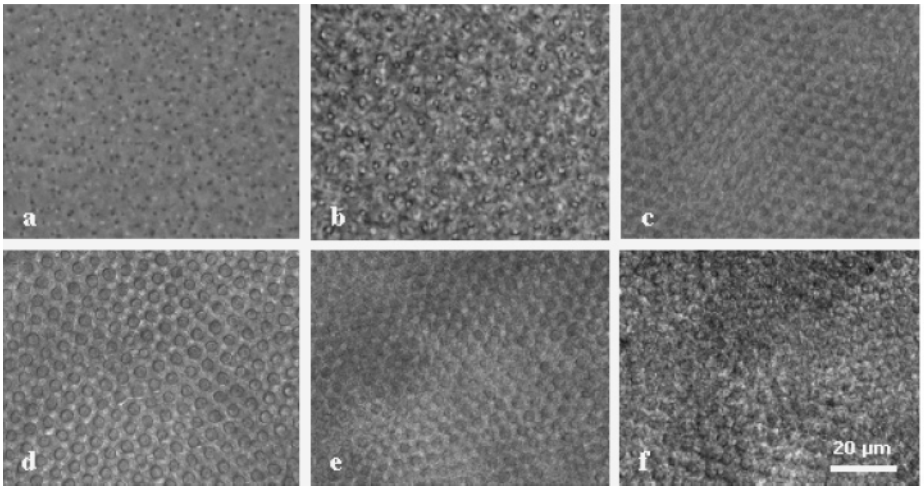

Figure 1. Phase contrast optical micrographs of morphological structures for sample of initial monomer weight fraction $w = 0.5$ at temperature $T = 100$ °C. Time $t = 24$ min (a), 2 h (b), 5 h (c), 12 h (d), 72 h (e), and 120 h (f).

product of Aldrich Chemical Co. (divinylbenzene content: 55%), and an inhibitor was removed by the same method as used for 4-chlorostyrene. Random copolymer of dimethylsiloxane and diphenylsiloxane (PDMSDPS) was purchased from Shin-Etsu Chemical Co. (catalog name KF54). The number-average molecular weight M_n and the diphenylsiloxane content in the copolymer were determined by ^{29}Si NMR (Bruker AV-600) to be 2.2×10^3 and 29 mol %, respectively. ^{1}H NMR gave a slightly different value, 27 mol %, to the diphenylsiloxane content. The approximate molecular weight distribution index was evaluated with a size-exclusion chromatograph instrument Waters 515 HPLC pump/2414 refractive index detector/Styragel columns HT2, HT3, and HT4 to be $(M_w/M_n)_r = 2.0$.[19]

After 4-chlorostyrene was mixed with poly(dimethylsiloxane-*co*-diphenylsiloxane) (PDMSDPS) at desired weight fraction, the mixture was stirred for 2 h at room temperature to ensure complete mixing. The sample mixture was sandwiched between a slide glass and a cover glass with poly(tetrafluoroethylene) spacer of 0.05 mm thickness. Polymerization and phase separation were made on a hot stage Linkam LTS350. Polymerization reaction was initiated by raising temperature without the aid of an initiator. Evolution of phase-separated domain structure was observed at reaction temperature 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 subsequent period. In addition to the video camera, a digital still camera with a 1704 × 2272 pixel detector was used to record high-resolution pictures of phase-separated domains.

The reaction conversion of 4CLS was evaluated from ultraviolet light absorption at the wavelength 255.4 nm, where the maximum absorption by 4CLS occurred. Absorption per unit weight k at this wavelength was determined in advance for each pure component, PDMSDPS, 4CLS, and its reaction product, poly(4-chlorostyrene) (P4CLS), in chloroform. PDMSDPS and P4CLS were found to have much smaller k than 4CLS (0.87% and 1.5% of 4CLS, respectively). Then, from the absorption by a reacted sample dissolved in chloroform (concentration was around 1×10^{-3} wt %), together with concentration of PDMSDPS and a sum of concentrations of 4CLS and P4CLS, the amount of 4CLS remaining in the reacted sample was calculated by using predetermined k's. Since a sufficiently large amount of the sample was necessary to obtain reliable values for the concentrations, we used a glass tube immersed in an oil bath as a reaction vessel instead of a combination of slide and cover glasses used for microscope observation. To examine the accuracy of the method, we evaluated 4CLS amount in a test mixture with known composition. A reasonable agreement (within 0.5%) was found at higher 4CLS content (65%), but the agreement deteriorated with decreasing the 4CLS content (within 20% at 10% 4CLS content) due to an error in subtracting the absorptions by P4ClS and PDMSDPS.

Change of a relative value of molecular weight $(M_w)_r$ of the reacted P4CLS with time was evaluated by size-exclusion chromatography using Waters Styragel columns HT3, HT5, and HT6E.

Results and Discussion

By continuous observation with a phase-contrast microscope for the first 12 h, the morphological development at initial monomer weight fraction $w = 0.5$ and temperature $T = 100$ °C was found as follows. Many small droplets, slightly smaller than 1 μm in diameter, appeared from an initially homogeneous mixture around time $t = 20$ min. These small droplets moved incessantly and frequently collided with each other. However, two colliding droplets did not coalesce into a larger droplet and were repelled after the collision. Also noticeable was a narrow distribution of droplet size, which made a marked contrast to a wide size distribution observed in PIPS of the other systems.[1,20] With a lapse of time, these droplets grew in size without broadening their size distribution as shown in Figure 1a,b. With the growth of the size, droplets became to occupy the large space in the mixture and gradually arranged themselves into an array. Around $t = 5$ h crystal-like regular arrays of droplets formed in places (Figure 1c). Arrays were bounded by dislocation lines (planes), and each region bounded by dislocation lines gradually increased in size over a period up to $t = 12$ h. At $t = 12$ h highly ordered array was clearly observed as shown in Figure 1d. The droplet size appreciably grew in a period from 5 to 12 h, but its growth rate seriously slowed down after 12 h. The number density of droplets, which was estimated from pictures shown in Figure 1, did not change so much (within 8% variance) over a period from $t = 24$ min to 12 h. Because of noncoalescence of droplets, this suggested that formation of droplets was restricted in a very early stage of phase separation. Phase separation behavior longer than 12 h was observed at intervals. At $t = 120$ h, regular arrays were partly destroyed, and droplets appeared to be distorted from the spherical shape. Morphological observation was repeated, and it was confirmed that morphological development was reproducible with relatively small variance in the time of initial appearance of droplets and the time of crystal-like array formation. However, the time when the array

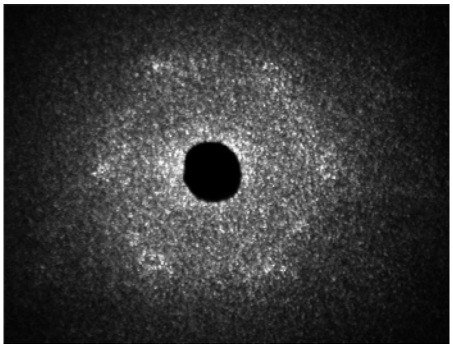

Figure 2. Laser diffraction pattern of a sample with initial monomer weight fraction $w = 0.5$ quenched after phase-separated at temperature $T = 100$ °C for 8 h. Wavelength of the incident laser beam was 532 nm.

was destroyed varied considerably from 48 to 120 h depending on sample.

A sample was taken out from the hot stage during its phase separation and quenched to room temperature. The regular array was not destroyed or changed by the quench, and the array structure of quenched sample did not show any appreciable change at room temperature for weeks. When laser light (wavelength = 532 nm) was impinged on a quenched sample, a diffraction pattern indicating regularity of the domain structure was observed as shown in Figure 2. We observed the domain structure at the bottom side of a quenched sample with an optical microscope and found the same regular array structure as observed from the topside, suggesting that the array extended three-dimensionally over the sample.

In the present system, phase separation was caused by segregation between the copolymer PDMSDPS and the reaction product, namely poly(4-chlorostyrene) (P4CLS). From microscope observations, it could not be decided whether PDMSDPS-rich phase or P4CLS-rich phase corresponded to the droplet. To clarify this, a PIPS experiment was carried out for a sample containing a cross-linking agent divinylbenzene (DVB) by an amount of 1% of the total weight under the same condition ($w = 0.5$, $T = 100$ °C). The addition of 1 wt % DVB did not qualitatively change the phase separation behavior including the formation of crystal-like regular array at least in the observed period. The reaction and phase separation were stopped at $t = 340$ min by quenching the temperature. After PDMSDPS and unreacted monomer/cross-linking agent were removed from the sample by washing with a large amount of cyclohexane twice, spherical droplets with narrow size distribution were obtained as shown in Figure 3, which clearly indicated that the P4CLS-rich phase corresponded to the droplet.

The conversion of 4-chlorostyrene monomer reacted at $w = 0.5$ and $T = 100$ °C is shown in Figure 4. The reaction conversion was very low at $t = 20$ min, when P4CLS-rich noncoalescing droplets appeared first. This indicated that the noncoalescing droplets consisted of viscous fluid rather than amorphous solid. Since the conversion was about 60% at $t = 5$ h, a fair amount of monomer remained in these droplets when they began to form the regular array. The data shown here were obtained for samples reacted in glass tubes because sufficiently large amounts of sample were necessary to obtain precise data, while the in situ microscope observations were made for samples reacted on slide glasses.

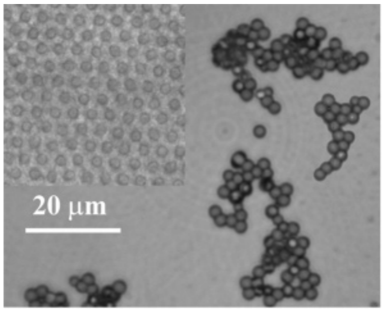

Figure 3. Optical micrograph of cross-linked particles obtained by polymerization-induced phase separation of a mixture containing divinylbenzene. PDMSDPS and unreacted monomer/divinylbenzene were removed by washing with cyclohexane. The inset is a phase contrast optical micrograph of in situ morphological structure ($t = 340$ min) before washing.

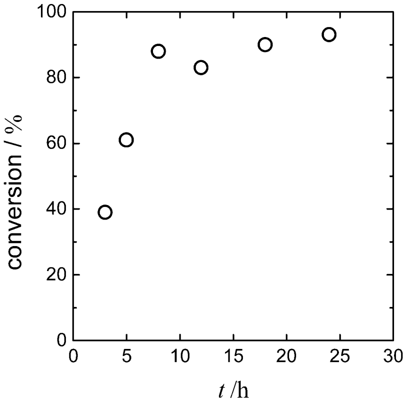

Figure 4. Temporal change of reaction conversion of 4CLS at $w = 0.5$ and $T = 100$ °C.

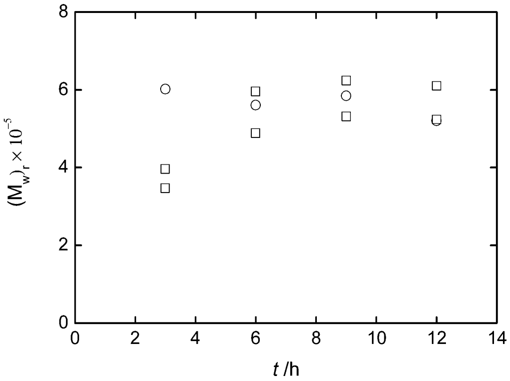

Figure 5. Relative molecular weights $(M_w)_r$ of poly(4-chlorostyrene) polymerized at $w = 0.5$ and $T = 100$ °C for a period of t in different reaction settings: in glass tube (○) and on slide glass (□).

The difference in the reaction setting might cause a slight change in reaction rate as suggested by molecular weight measurements as shown in Figure 5. In the figure, we used the molecular weight in equivalence to polystyrene standards, since our concern laid in examining reproducibility of the data in different reaction settings rather than obtaining the absolute value of molecular weight. At longer reaction times, data were reasonably reproducible and showed no dependence on reaction setting or reaction time as expected. However, a smaller molecular weight value was obtained when the samples were reacted on slide glasses for 3 h. Production of polymers with lower molecular weights in an earlier period was probably caused by the impurities inhibiting the radical reaction because a sample on

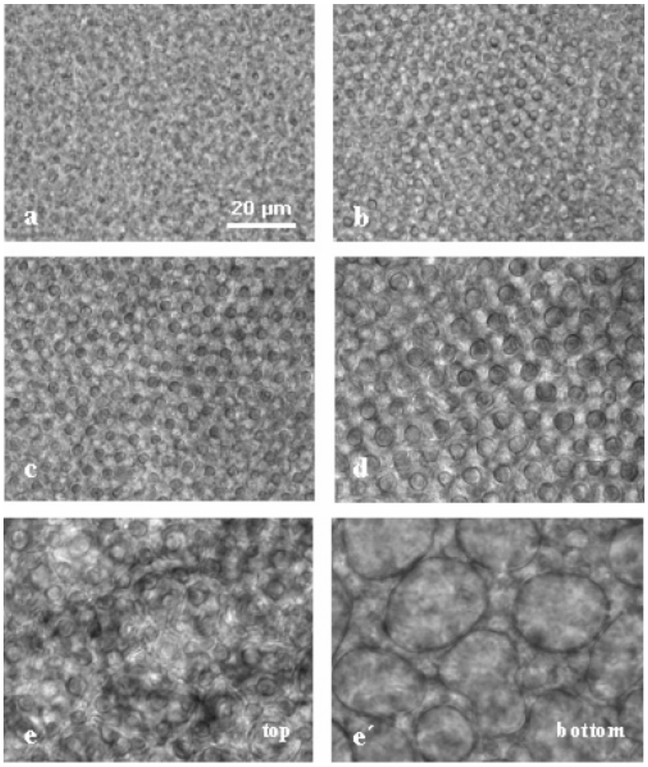

Figure 6. Phase contrast optical micrographs of morphological structures at t = 12 h and T = 100 °C for initial compositions $w = 0.2$ (a), 0.3 (b), 0.4 (c), 0.6 (d), and 0.7 (e); 0.7, observed from bottom side (e′).

a slide glass was more vulnerable to contamination during its preparation process. The impurities might change the reaction rate as well, and therefore Figure 4 might not show the exact temporal change of conversion during microscope observation. However, it was obvious that P4CLS-rich droplets observed in early period contained a considerable amount of monomers, since a sufficiently large amount of monomer had to remain at 3 h in order for the average molecular weight to increase during a period from 3 to 6 h.[21]

The morphological development was also studied at several different initial monomer compositions with temperature being fixed at 100 °C. The formation of the crystal-like array was observed for initial compositions w = 0.3, 0.4, and 0.6 as shown in Figure 6b–d. The process that the regular array formed through at these compositions was qualitatively the same as the one at $w = 0.5$: Droplets with nearly uniform size distribution appeared initially and grew without coalescence, leading to the formation of crystal-like arrays. A quantitative difference laid in the growth rate of droplets. At higher w, droplets grew faster, as reflected in the difference of droplet size in Figure 6. At $w = 0.2$, droplets with a narrow size distribution appeared but regular array did not form in the investigated period (36 h). The droplet size and the total volume occupied by droplets remained relatively small over this period. At $w = 0.7$, droplets appeared, but they showed a wide distribution in size from their first appearance. The coalescence of domains occurred as illustrated by consecutive pictures in Figure 7. No regular structure formed in the subsequent period and large flat domains formed at the bottom of the mixture (Figure 6e,e′).

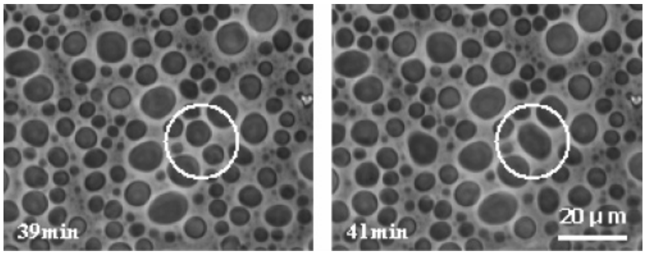

Figure 7. Morphological structures at the bottom of sample of $w = 0.7$ at 100 °C. Time is indicated in the figure. Coalescence of two domains in the circle is observed.

The temperature dependence of morphological development was investigated at a fixed initial composition of $w = 0.5$. At all temperatures investigated in the range from 90 to 130 °C, droplets formed, and the growth rate of droplets increased with increasing temperature. At lower temperatures, namely T = 90, 110, and 120 °C, crystal-like regular arrays similar to those observed at T = 100 °C formed. At T = 125 °C regular arrays formed only in limited regions, and they coexisted with droplets being distributed irregularly in space as shown in Figure 8. Much larger nonspherical domains were also observed. When temperature was increased further to T = 130 °C, regular arrays no longer formed and large flat domains formed at the bottom of the mixture. The structure was quite similar to the one observed at w = 0.7 and T = 100 °C shown in Figure 6e.

At $w = 0.5$, the regular array formed in a lower temperature range. The similar temperature dependence was expected to hold at the other initial compositions w, and this was confirmed by experimental observations made in the range from w = 0.3 to 0.7. Temperatures and compositions at which the regular array was observed are summarized in Figure 9. At all w, the regular array formed at lower temperatures. A boundary that separated two temperature regions where only and no regular array exist respectively extended over several degrees, and in the boundary temperature range the regular array of droplets coexisted with irregularly distributed droplets. The boundary temperature decreased linearly with increasing initial composition.

Figure 10 shows a plot of the time t_{ra} when the regular array was first observed against w and T. At a fixed initial composition, t_{ra} decreased with increasing temperature. At a fixed temperature, t_{ra} increased with decreasing initial composition, and especially in a range of $w < 0.3$, a steep increase was observed. Though no regular array was observed to form in initial 36 h at w = 0.2 and T = 100 °C as mentioned above, the composition dependence at higher temperatures suggested that regular array would appear after sufficiently longer phase separation time at this experimental condition. However, at further low composition of w = 0.1, the regular array formation was not observed even at 140 °C in 24 h, which implied that t_{ra} diverged somewhere between w = 0.1 and 0.2. As already seen in the development of phase-separated domains, regular arrays did not form at low volume fractions of droplets. Since the total volume of droplet phase at 100% conversion was a decreasing function of initial monomer composition, it became too small to form the regular array at very low initial monomer compositions. This explained the divergence of t_{ra} or existence of lower boundary of w for the array formation.

It was found that the formation of a crystal-like array was always preceded by the appearance of noncoalescing droplets with a narrow size distribution. This implies

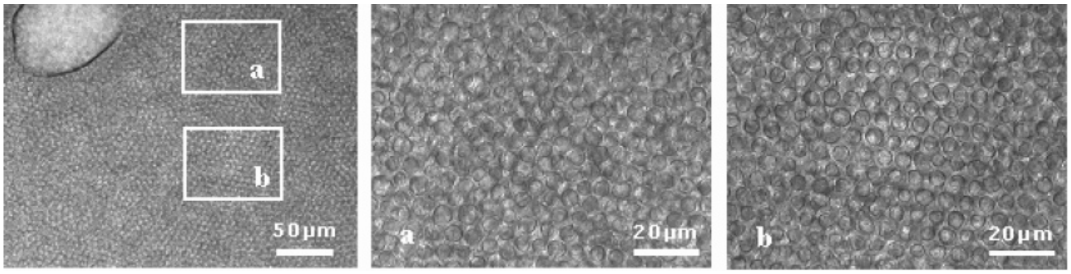

Figure 8. Phase contrast optical micrographs of morphological structures of sample with $w = 0.5$ kept at $T = 125$ °C for $t = 22$ h. Panels a and b are magnified views of framed parts in the left panel.

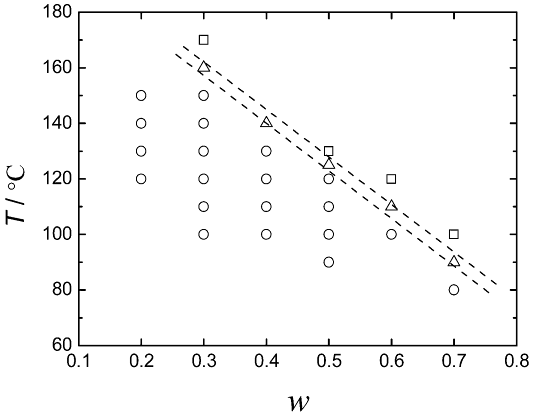

Figure 9. Morphological structures observed at temperature T and initial monomer weigh fraction w: crystal-like arrays (○), regular arrays coexisted with irregularly distributed droplets and large domains (△), and droplets with wide size distribution coexisted with large domains (□). Lines are only to guide the eye.

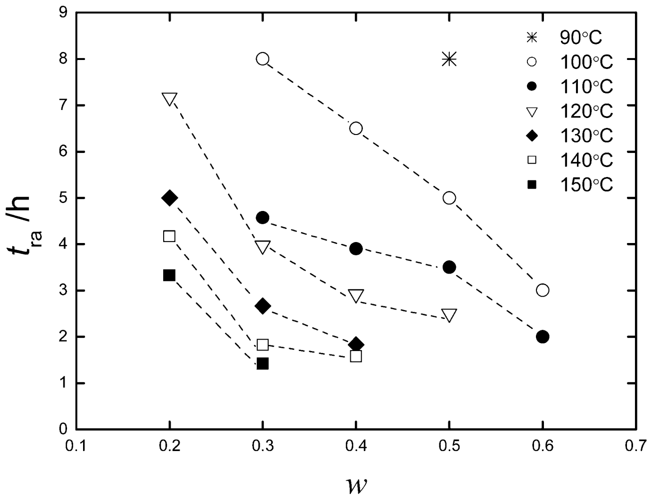

Figure 10. Time t_{ra} when the regular arrays are first observed for various initial monomer weigh fraction w and temperature T. Lines are only to guide the eye.

that the appearance of noncoalescing droplets with a narrow size distribution has a fundamental importance in the array formation. It has been observed that noncoalescing droplets form in phase separation of nonreacting system.[22,23] When a mixture of components having largely different viscoelastic properties is deep quenched with an off-critical composition on the low viscoelastic component-rich side of the phase diagram, the higher viscoelastic phase forms droplets, and these droplets move rapidly and collide with each other without coalescing. Suppression of coalescence in a mixture consisting of components with such asymmetric viscoelasticity is explained by a long characteristic time of chain entanglement in the higher viscoelastic phase compared with the characteristic collision time of two droplets. Dynamics of coalescence depends greatly on viscoelastic properties of the droplet phase because the diffusion of polymer chains through the contact surface between two droplets is necessary in order for the coalescence to happen. On the other hand, the time span during which the two droplets are in contact depends very much on the viscoelasticity of the surrounding fluid. Therefore, in the case that droplets have much higher viscoelastic properties than the surrounding fluid, the time required for coalescence to occur is much longer than the contact time, resulting in the suppression of coalescence. Recent studies on nonreacting systems have revealed that, besides emergence of noncoalescing droplets, asymmetry in viscoelastic properties between demixing components has significant effects on phase separation dynamics because of the coupling between concentration diffusion and viscoelastic stress[22–27] and that a mixture of components having largely different viscoelastic properties is described by a new class of dynamic model that has not been given in the classification by Hohenberg and Halperin.[28] P4CLS had much longer chain length and much higher glass transition temperature ($T_g = 130$ °C) than PDMS-DPS ($T_g <$ room temperature), and therefore there was a large difference in viscoelasticity between two segregating components in the present system. It was reasonable to consider that the difference in viscoelasticity had significant effects on phase separation dynamics of both reacting and nonreacting systems. This was supported by experimental results that coalescence of droplets occurred at higher temperatures and higher initial monomer compositions because the viscoelastic difference between two phases at early period of phase separation decreased with either increasing temperature or monomer composition.

A narrow size distribution of droplets has been also observed in the viscoelastic phase separation of a nonreacting mixture, and its physical origin has been explained as follows. The distribution of droplet size is considered to reflect the distribution of concentration fluctuation wavelength in the spinodal decomposition that precedes the formation of droplets. As is well-known, the wavelength distributes around a single dominant value in the spinodal decomposition. In contrast to the suppression of coalescence of droplets, the connection between the narrow size distribution in the reacting system and that in the nonreacting system is not so clear. In the nonreacting system, the droplets with narrow size distribution were generated by a deep quench in the unstable state at an off-critical composition. In PIPS, the thermodynamic state gradually changed with proceeding of the reaction, and the mixture inevitably went through the metastable state before it reached the unstable state. In phase separation from the metastable state, droplets with a wide size distribution will be generated through the nucleation and growth mechanism. Therefore, in our system the nucleation and growth must be quite slow compared with polymerization reaction so that the system must go into unstable region rather quickly after the polymerization process begin and resulting into a narrow size distribution in the early stage of the process PIPS.

Even in the case that droplets with a wide size distribution initially formed by the nucleation and growth mechanism, a narrow size distribution would be produced in a later period if there existed a mechanism by which a small droplet grew faster than a large droplet in PIPS. However, such narrowing process of droplet size distribution did not seem consistent with our observations. The distribution was always narrow from the beginning when the phase-separated droplets start to appear. Because of suppression of coalescence, each droplet probably grew by absorbing monomers and adsorbing isolated P4CLS chains on the surface. The rate of either process was considered to be a function of droplet size with other conditions being equal for all droplets at any given time, and thus the growth rate was expected to be identical for droplets of equal size. Formation of new droplets by newly produced polymer chains was probably quite rare because of the very slow nucleation rate of droplets, which we assumed above to explain the initial narrow size distribution. Rapidly moving droplets adsorbed P4CLS chains before these chains formed a stable P4CLS-rich nucleus. In other words, the narrow distribution of droplet size, which was generated in an early period of phase separation, would be maintained through the subsequent growth process of droplets. The speculated mechanism of formation of droplets with narrow size distribution given here was based on assumptions that had not been confirmed experimentally yet, and it admitted other explanations. Probably it is worthwhile to mention that a regular array of droplets with narrow size distribution has been observed in "breath figure" formation on the surfaces of volatile fluids, though the connection between these two similar observation is not clear at present.[29,30]

Since there did not seem to be a strong attractive interaction between droplets, the crystal-like array of fluid droplets was conceived to formed by a mechanism closely analogous to the mechanism by which hard spheres formed a crystal array. Hard spheres of a uniform diameter are known to undergo a fluid-to-solid phase transition, referred to as the Alder transition, as the density increased.[31,32] The transition was first found in a computer simulation for a two-dimensional hard disk liquid and was later observed in an experiment for a polymer latex solution.[33] Viscoelastic fluid droplets resembled hard spheres in that they did not coalesce by collision. Therefore, it is highly probable that noncoalescing fluid droplets with narrow size distribution undergo a structure transition with increasing volume fraction of droplets. In fact, the regular array did not form at low w, where the volume fraction of droplet phase was low.

In PIPS, the overall molecular composition was not fixed in the phase separation process, and the volume fraction of droplets increased considerably with the proceeding of polymerization reaction. This accounts for why the crystal-like array formed in PIPS while it did not in the nonreacting system. In the viscoelastic phase separation of a nonreacting system, noncoalescing moving droplets form only at small volume fractions of higher viscoelastic phase, which are considered to be much smaller than the critical volume fraction for the transition to the crystal-like structure. In a phase separation induced by radical polymerization, even if the final volume fraction of the higher viscoelastic component is larger than the critical value for the Alder-type transition, the volume fraction in an early period of phase separation can be small enough to produce moving droplets, since the mixture is usually destabilized on the nonreacting component-rich side of phase diagram.[15,34] We observed that the transition occurred earlier as the initial monomer composition increased. This is reasonable because a mixture containing larger amount of monomer can reach the critical volume fraction at a lower reaction conversion.

Since the P4CLS-rich droplet was not a real hard sphere, it would be distorted or coalesced when the volume fraction increased over the close-pack value of a sphere. In fact, we observed that the regular array was broken after quite long phase separation time.

In the latex solution the transition was reported to occur at the volume fraction of 0.5.[33] The volume fraction estimated from apparent droplet size and distance between two droplets was much smaller than 0.5 in some case. For example, the volume fraction of droplets estimated by assuming the hexagonal structure for the array shown in Figure 6c was as small as 0.1. However, the estimated volume fraction was not sufficiently reliable. A clear image of droplets could be obtained only in a quite limited range of focal depth, and therefore there was a possibility that the optical micrographs did not show the largest cross section of droplets. Therefore, the significance of the quantitative discrepancy in the volume fraction is not clear at present.

Conclusions

A liquid−liquid phase separation was induced by radical polymerization of 4-chlorostyrene monomer in the presence of random copolymer poly(dimethylsiloxane-*co*-diphenylsiloxane) and poly(4-chlorostyrene)-rich phase formed droplets. Under certain conditions of initial monomer concentration and temperature, these droplets exhibited a quite narrow size distribution and hardly coalesced by collisions. The behavior was highly resembles that observed in the moving droplet phase of viscoelastic phase separation of nonreacting systems, although a volume fraction of droplets was much higher in the present system.

Poly(4-chlorostyrene) produced by the reaction had much longer chain length and a glass transition temperature than the copolymer PDMSDPS, and consequently a large difference in viscoelastic properties between the segregating components existed in this system. Therefore, the results indicated that the interplay between the dynamical asymmetry and the growth of concentration fluctuation had significant effects on the morphological development in phase separation induced by polymerization reaction as well. With growth of the droplet size, droplets gradually filled the space and spontaneously arranged themselves in a regular array like a crystal. Such crystal-like array structure formed over wide initial monomer composition and temperature ranges. The boundary temperature, above which the regular array did not form, decreased with increasing initial monomer composition. At sufficiently low compositions (<0.2), droplets with narrow size distribution appeared but they did not form the regular array.

Mechanisms for regular array formation were speculated as follows. Polymerization reaction rapidly proceeded initially, and the system went into the unstable region before the nucleation and growth of 4CLS-rich droplets proceeded Network structure formed by spinodal decomposition at early stage of phase separation broke up into droplets with narrow size distribution. Because of viscoelastic asymmetry, coalescence of droplets was suppressed, and droplets grew by absorbing monomer and adsorbing newly produced polymer chains. Nucleation of new droplets in the copolymer-rich continuous domain was very slow, and the size distribution remained to be narrow during growing process of droplets. With growth of droplet size, the volume fraction of droplets in the mixture increased. Owing to noncoalescing nature of fluid droplets, the Alder-type "fluid-to-solid" transition occurred, and the regular array was formed.

Although the fluid-to-solid transition combined with viscoelastic phase separation qualitatively accounts for the basic aspects of the regular array formation, the speculated mechanisms were based on several assumptions whose validity was not confirmed yet. To acquire further understanding of the mechanism of the regular array formation, qualitative analyses, for instance of the volume fraction of droplets, are necessary. It is also important to clarify whether the regular array formation is specific to this system or general to a system where dynamical asymmetry exists. Although the detailed mechanism of this phenomenon is not full understood yet, the present results show that a viscoelastic asymmetry causes a quite unique morphological development in polymerization-induced phase separation.

Acknowledgment. This work has been supported by the Chinese Academy of Sciences (Grant KJCX2-SW-H07), the Ministry of Science and Technology of China (Grant 2003CB615600), and the Chinese National Science Foundation (Project 20490220). The authors thank Yangping Zhu for his analysis of ^{29}Si NMR data and Prof. Yongming Chen for the use their SEC.

References and Notes

(1) Inoue, T. *Prog. Polym. Sci.* **1995**, *20*, 119.
(2) Williams, R. J. J.; Rozenberg, B. A.; Pascault, J. P. *Adv. Polym. Sci.* **1997**, *128*, 95.
(3) Ishii, Y.; Ryan, A. J. *Macromolecules* **2000**, *33*, 158.
(4) Jansen, B. J. P.; Rastogi, S.; Meijer, H. E. H.; Lemstra, P. J. *Macromolecules* **2001**, *34*, 3998.
(5) Ritzenthaler, S.; Court, F.; David, L.; Girard-Reydet, E.; Leibler, L.; Pascault, J. P. *Macromolecules* **2002**, *35*, 6245.
(6) Loera, A. G.; Cara, F.; Dumon, M.; Pascault, J. P. *Macromolecules* **2002**, *35*, 6291.
(7) Hoppe, C. E.; Galante, M. J.; Oyanguren, P. A.; Williams, R. J. J. *Macromolecules* **2002**, *35*, 6324.
(8) Schierholz, J. U.; Hellmann, G. P. *Polymer* **2003**, *44*, 2005.
(9) Keizer, H. M.; Sijbesma, R. P.; Jansen, J. F. G. A.; Pasternack, G.; Meijer, E. W. *Macromolecules* **2003**, *36*, 5602.
(10) Rebizant, V.; Abetz, V.; Tournilhac, F.; Court, F.; Leibler, L. *Macromolecules* **2003**, *36*, 9889.
(11) Wang, M.; Yu, Y.; Wu, X.; Li, S. *Polymer* **2004**, *45*, 1253.
(12) Tran-Cong, Q.; Harada, A. *Phys. Rev. Lett.* **1996**, *76*, 1162. Harada, A.; Tran-Cong, Q. *Macromolecules* **1997**, *30*, 1643.
(13) Echte, A. *Angew. Makromol. Chem.* **1977**, *58/59*, 175.
(14) Fischer, M.; Hellmann, G. P. *Macromolecules* **1996**, *29*, 2498.
(15) Tanabe, T.; Furukawa, H.; Okada, M. *Polymer* **2003**, *44*, 4765.
(16) Okada, M.; Masunaga, H.; Furukawa, H. *Macromolecules* **2000**, *33*, 7238.
(17) Furukawa, H. *J. Phys. Soc. Jpn.* **1994**, *63*, 3744, 3919.
(18) Matsushita, Y.; Furukawa, H.; Okada, M. *Phys. Rev. E* **2004**, *70*, 040501.
(19) An incorrect value of $(M_w/M_n)_r$ was given in ref 18. The value was obtained carelessly with using a SEC that did not fit well for low molecular weight range. Therefore, polystyrene-equivalent molecular weight given in ref 18 was also incorrect.
(20) Okada, M.; Fujimoto, K.; Nose, T. *Macromolecules* **1995**, *26*, 1795.
(21) The reaction conversions presented here were quantitatively different from those given in ref 18, and a much smaller molecular weight of the reaction product was obtained in the previous work. The origin of such large discrepancy was not clearly understood. Difference in determination method of the conversion (size exclusion chromatography was used previously) did not account for such large difference. Probably the sample used in the previous work contained impurities such as moisture that prohibited the reaction. Despite the discrepancy in conversion and molecular weight, the discussion made in the previous report was not affected.
(22) Tanaka, H. *Macromolecules* **1992**, *25*, 6377.
(23) Tanaka, H. *Phys. Rev. Lett.* **1993**, *71*, 3158.
(24) Tanaka, H. *J. Phys.: Condens. Matter* **2000**, *12*, R207. Tanaka, H. *J. Chem. Phys.* **1994**, *100*, 5323.
(25) Aubert, J. H. *Macromolecules* **1990**, *23*, 1446.
(26) Song, S. W.; Torkelson, M. *Macromolecules* **1994**, *27*, 6390.
(27) Taniguchi, T.; Onuki, A. *Phys. Rev. Lett.* **1996**, *77*, 4910.
(28) Hohenberg, P. C.; Halperin, B. I. *Rev. Mod. Phys.* **1976**, *49*, 435.
(29) Srinivasarao, M.; Collings, D.; Philips, A.; Patel, S. *Science* **2001**, *292*, 79.
(30) Limaye, A. V.; Narhe, R. D.; Dhote, A. M.; Ogale, S. B. *Phys. Rev. Lett.* **1996**, *76*, 3762.
(31) Alder, B. J.; Wainright, T. E. *Phys. Rev.* **1962**, *127*, 359.
(32) Alder, B. J.; Hoover, W. G.; Young, D. A. *J. Chem. Phys.* **1968**, *49*, 3688.
(33) Kose, A.; Hachisu, S. *J. Colloid Interface Sci.* **1974**, *46*, 460.
(34) Okada, M.; Inoue, G.; Ikegami, T.; Kimura, K.; Furukawa, H. *Polymer* **2004**, *45*, 4315.

MA050896Y