Notes

Polymerization-Induced Phase Separation of Styrene and Its Derivatives: Rarity of Crystal-like Array Formation

Xin Wang, Mamoru Okada,* and Charles C. Han*

State Key Laboratory of Polymer Physics and Chemistry, Joint Laboratory of Polymer Science and Materials, Beijing National Laboratory for Molecular Sciences, Institute of Chemistry, Chinese Academy of Sciences, Zhongguancun, Haidian, Beijing 100080, P. R. China

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Introduction

We found recently that spherical domains (droplets) being roughly uniform in size spontaneously arranged themselves to form a crystal-like array during the liquid−liquid phase separation induced by radical polymerization of 4-chlorostyrene monomer in the presence of random copolymer of dimethylsiloxane and diphenylsiloxane (PDMSDPS).[1,2] In a period precedent to the array formation, it was always observed that poly(4-chlorostyrene)-rich droplets hardly coalesced by their collisions. Since noncoalescing droplets with narrow size distribution are known to be characteristic of the viscoelastic phase separation at low concentration of higher viscoelastic components,[3,4] it is considered that a large difference in viscoelastic property between poly(4-chlorostyrene) and PDMSDPS plays a key role in the formation of the crystal-like array. Then, the spontaneous ordering of noncoalescing droplets was understood as a phenomenon analogous to the fluid-to-solid transition of hard spheres with uniform size.[5,6] On the other hand, when *n*-butyl methacrylate was used as monomer instead of 4-chlorostyrene, no crystal-like array formed, and coalescing droplets, spongelike, and network domain structures formed depending on the initial monomer concentration.[7] Since the spongelike and network domains are also characteristic of the viscoelastic phase separation of the nonreacting system,[4,8] viscoelastic asymmetry existed in the *n*-butyl methacrylate system as well. In other words, the viscoelastic asymmetry between two demixing phases is not sufficient for the crystal-like array to form in polymerization-induced phase separation (PIPS). In the present work, mixtures of styrene derivatives and PDMSDPS were studied to examine the generality of the crystal-like array formation in PIPS.

Experimental Section

Styrene was purchased from Beijing Chemical Co., and 2-chlorostyrene, 4-methylstyrene, and 4-bromostyrene were from Acros Organics. Monomers were purified by distillation under reduced pressure after washed with 10% sodium hydroxide aqueous solution to remove the inhibitor. The random copolymer of dimethylsiloxane and diphenylsiloxane, the same material as used in the previous paper,[2] with a diphenylsiloxane content of 29 mol % was purchased from Shin-Etsu Chemical Co. (product name KF 54). Its number-average molecular weight was $M_n = 2.2 \times 10^3$, and the approximate molecular weight distribution index was $M_w/M_n = 2.0$.

Experimental methods used in this work were almost the same as in the previous work.[2] Thus, we described them only briefly here. Radical polymerization was initiated by raising temperature without the aid of initiator. Experiments were carried out at a fixed monomer molar fraction $x = 0.94$ and temperature $T = 100$ °C, unless otherwise stated. Evolution of phase-separated domain structure of a 0.05 mm thick sample, which was placed on a hot stage Linkam LTS350, was observed with a phase-contrast microscope Olympus BX51. The reaction conversion was determined from the maximum ultraviolet absorption of a monomer. The relative molecular weight $(M_w)_r$ of the polymerization product was measured by a size-exclusion chromatograph apparatus (Waters Alliance 2000 with columns HT6E and HT2).

Results and Discussion

Figure 1 shows the time evolution of phase-separated domains of the 2-chlorostyrene (2ClS)/PDMSDPS system. The molar fraction of the monomer $x = 0.94$ corresponds to the weight fraction $w = 0.5$. Small droplets formed around $t = 5$ min after the reaction was initiated by temperature jump. In contrast to the case of the isomer 4-chlorostyrene (4ClS) reacted under the same condition, these droplets coalesced easily by their collisions. Coalescence caused broadening of the distribution of droplet size and prevented formation of a crystal-like array. Eventually, larger droplets precipitated on the bottom of the sample cell, and the precipitated droplets coalesced to form quite large flat domains (not shown here). The phase separation of the 2ClS system was faster than that of the 4ClS system: In the 4ClS system, the induction time (that is, the time lapsed from the beginning of the reaction to the first appearance of domains) was 20 min, and it took about 480 min for the droplet size to become about 3.5 μm.

In the 4ClS system the crystal-like array formed from $w = 0.2$ ($x = 0.80$) to $w = 0.6$ ($x = 0.96$) at 100 °C, and the maximum composition where the array formed decreased with increasing temperature. The morphological development observed for the 2ClS rather resembled those of the 4ClS system in a range of higher monomer concentration and higher temperature. Therefore, we examined phase separation behavior of the 2ClS system at lower compositions and a lower temperature: $x = 0.75$ and 0.90 at $T = 100$ °C; $x = 0.75$, 0.90, and 0.94 at $T = 90$ °C. However, morphological developments were similar to shown in Figure 1, and neither crystal-like arrays nor noncoalescing droplets were observed.

Styrene (St) and 4-methylstyrene (4MeS) showed morphological developments similar to that of 2-chlorostyrene: Droplets coalesced, and no regular array formed. The induction times were 10 min in St and 60 min in 4MeS, but in both systems droplets grew faster than in the 4ClS system and precipitated around 100 min.

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* To whom correspondence should be addressed: Ph +86 10 82618089; Fax +86 10 62521519; e-mail: m.okada@iccas.ac.cn and c.c.han@iccas.ac.cn.

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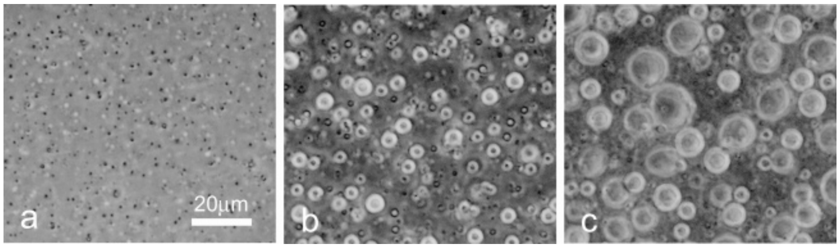

Figure 1. Morphological development of 2-chlorostyrene/PDMSDPS mixture at $x = 0.94$ and $T = 100$ °C: (a) 6, (b) 30, and (c) 100 min.

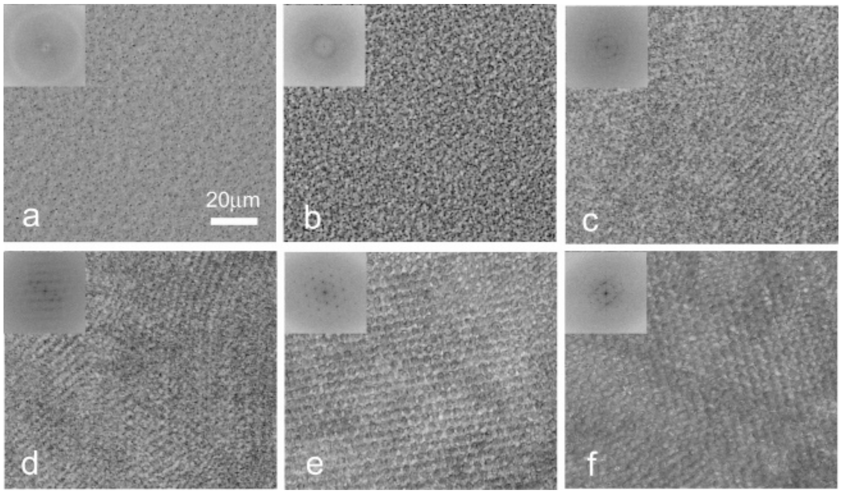

Figure 2. Morphological development of 4-bromostyrene/PDMSDPS mixture at $x = 0.94$ and $T = 100$ °C: (a) 16, (b) 60, (c) 140, (d) 170, (e) 480, and (f) 1440 min. Insets show Fourier transform of optical micrograph images.

Figure 2 shows the morphological development of the 4-bromostyrene (4BrS)/PDMSDPS system. Moving droplets with a narrow size distribution appeared around $t = 9$ min, and the coalescence of droplets was observed to be suppressed. The droplets grew in size without broadening the size distribution, and arrays of droplets formed locally around $t = 140$ min. With a lapse of time, the order of structure increased as depicted by the Fourier transform of micrograph images, shown in the insets of the figures. The array structure was partially broken after a quite long time ($t = 1440$ min). In the 4BrS system, the arrays began to form earlier than in the 4ClS system (300 min), and the size of droplets (2 μm) forming the array was slightly smaller than that (3.5 μm) in the 4ClS system.

Out of four styrene and its derivatives studied in this work, only one monomer formed the crystal-like array. Especially it was noted that two isomers of chlorostyrene formed different morphological structures. Thus, the array formation was considered a rather rare phenomenon. We discuss, below, the controlling factors of the array formation by comparing three systems of 4ClS, 2ClS, and 4BrS.

Phase separation behavior of the 2ClS system appeared rather "normal", that is, nonviscoelastic. Viscoelasticity of a material is reflected in the glass transition temperature T_g and increases with the molecular weight. The glass transition temperature of poly(2-chlorostyrene) (P2ClS) is 392 K and is roughly the same as T_g of poly(4-chlorostyrene) (P4ClS), 388−401 K, and poly-(4-bromostyrene) (P4BrS), 391 K.[9] The relative molecular weights $(M_w)_r$ of P2ClS, P4ClS, and P4BrS polymerized for $t = 12$ h at $x = 0.94$ and $T = 100$ °C were 4.0×10^5, $(5.0-6.1) \times 10^5$, and 4.8×10^5, respectively. The relative molecular weight of P2ClS was slightly smaller than those of the other two polymers, but the difference was very small compared with the difference between $(M_w)_r$ of these polymers and PDMSDPS. Therefore, neither T_g nor $(M_w)_r$ did not account for the "normal" phase separation behavior of the 2ClS system. Viscoelasticity of a phase depends not only on viscoelasticity of each component molecule but also on its concentration. The concentrations of demixing phases are determined by segregation strength of the components. The segregation strength between the product polymer and PDMSDPS will be discussed in a later section.

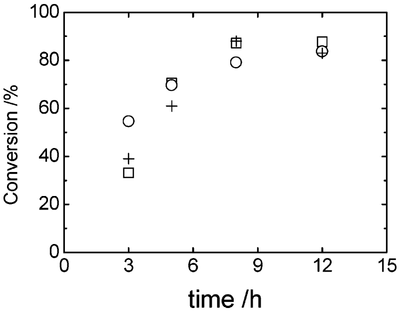

Figure 3. Temporal change of reaction conversions of monomer in PDMSDPS mixture at $x = 0.94$ and $T = 100$ °C: 2ClS (○), 4BrS (□), and 4ClS (+).

In a nonreactive system, viscoelastic phase separation is known to occur by a deep quench.[4] In a polymerization-induced phase separation, the quench depth changes with proceeding of the reaction. Thus, if phase separation is much faster than the reaction, the phase separation always proceeds in a shallow quench region, and the separation dynamics is expected to be normal. So, the reaction must be sufficiently fast so that the viscoelastic phase separation occurs in polymerization-induced phase separation. Figure 3 shows the temporal change of the reaction conversions. Contrary to our expectation, the early period reaction rate of 2-chlorostyrene appeared to be slightly faster than that of the other two monomers. Thus, the reaction rate was not a main factor accounting for the difference between 2ClS and the other two monomers that formed the crystal-like array.

Another conceivable origin is the segregation strength between demixing components. Since the high reactivity of a monomer at the experimental temperature made it extremely difficult to measure the phase diagram of a monomer/product polymer/PDMSDPS solution, the solubility parameter δ calculated by the group contribution method was used as a measure of the segregation strength. There are several methods to evaluate δ, and we calculated it based on Hoy's system,[10,11] which distinguished between two isomers of chlorostyrene, and obtained $\delta_{\mathrm{P4ClS}} = 20.47\ \mathrm{J}^{1/2}\ \mathrm{cm}^{-2/3}$, $\delta_{\mathrm{P2ClS}} = 19.89\ \mathrm{J}^{1/2}\ \mathrm{cm}^{-2/3}$, $\delta_{\mathrm{P4BrS}} = 20.27\ \mathrm{J}^{1/2}\ \mathrm{cm}^{-2/3}$, $\delta_{\mathrm{PS}} = 19.35\ \mathrm{J}^{1/2}\ \mathrm{cm}^{-2/3}$, and $\delta_{\mathrm{P4MeS}} = 19.86\ \mathrm{J}^{1/2}\ \mathrm{cm}^{-2/3}$ (here included were the values of polystyrene (PS) and poly(4-methylstyrene) (P4MeS)). The parameter of PDMSDPS was not evaluated because the group contribution of silicon was not available in Hoy's system. However, a simpler method, that is, Small's equation $\delta = (E_{\mathrm{coh}}/V)^{1/2}$,[12] with Fedors' tabulated values of the group contributions to molar cohesive energy E_{coh} and molar volume V,[11,13] gave $\delta_{\mathrm{PDMSDPS}} = 18.00\ \mathrm{J}^{1/2}\ \mathrm{cm}^{-2/3}$, $\delta_{\mathrm{P4ClS}} = \delta_{\mathrm{P2ClS}} = 23.80\ \mathrm{J}^{1/2}\ \mathrm{cm}^{-2/3}$, $\delta_{\mathrm{P4BrS}} = 23.92\ \mathrm{J}^{1/2}\ \mathrm{cm}^{-2/3}$, $\delta_{\mathrm{PS}} = 21.59\ \mathrm{J}^{1/2}\ \mathrm{cm}^{-2/3}$, and $\delta_{\mathrm{P4MeS}} = 21.11\ \mathrm{J}^{1/2}\ \mathrm{cm}^{-2/3}$, and consequently it was reasonable to consider that $\delta_{\mathrm{PDMSDPS}}$ was smaller than the above values. This was reasonable because the strong segregation caused a large difference in the product polymer concentration between two demixing phases and as its consequence a large dynamic asymmetry. It was noticed that the two polymers producing the array had higher δ than the remaining three polymers. Therefore, it was suggested that segregation had to be quite strong to form a regular array.

Conclusion

It was found the 4-bromostyrene system formed crystal-like array, revealing that the array formation was not specific to the 4-chlorostyrene system. However, in the styrene, 2-chlorostyrene, and 4-methylstyrene systems no regular array formed, suggesting that the array formation was a rather rare phenomenon. Neither the viscoelastic properties of the polymerization products nor the reaction rates of monomers reasonably accounted for the difference in phase-separated domain structure between these two groups. The solubility parameter evaluated on the basis of the group contribution method suggested that the strong segregation between the demixing components was an origin of the crystal-like structure formation.

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