Crystal-like pattern formation in polymerization-induced phase separation

Yuichiro Matsushita

Department of Polymer Chemistry, Tokyo Institute of Technology, Ookayama, Meguro-ku, Tokyo 152-8552, Japan

Hidemitsu Furukawa

Division of Biological Sciences, Graduate School of Science, Hokkaido University, N8, W5, North Ward, Sapporo 060-0810, Japan

Mamoru Okada*

Joint Laboratory of Polymer Science and Materials, Institute of Chemistry, Chinese Academy of Sciences, Zhongguancun, Haidian, Beijing 100080, People's Republic of China

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). Droplets with a 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 in a regular array like a crystal. The mechanism of regular array formation was discussed based on the large difference in viscoelastic properties between two segregating components.

Various patterns that form in phase separation of initially homogeneous mixtures have been widely studied as an important subject of nonequilibrium statistical mechanics. In phase separation associated with chemical reaction, the interplay between phase separation and reaction increases the variety of patterns and produces remarkable patterns in some cases. In phase separation induced by polymerization reaction or crosslinking reaction, several interesting patterns have been reported as well [1–7]. Marked examples are the concentric pattern appearing in phase separation induced by photocrosslinking of random copolymer poly(styrene-co-chloromethylstyrene) in the presence of poly(vinylmethylether) [3,4], and the salami pattern appearing in high-impact polystyrene [5,6] or in radical polymerization of 2-chlorostyrene in the presence of polystyrene [7]. In this paper, we reported a unique structure formed during phase separation induced by radical polymerization of 4-chlorostyrene monomer in the presence of random copolymer poly(dimethylsiloxane-co-diphenylsiloxane). The newly found pattern exhibited high regularity, which made a striking contrast to previously known patterns of polymerization-induced phase separation. Such a highly regular pattern was quite unexpected for liquid-liquid phase separation of a mixture, where no block copolymer was contained.

Sample monomer 4-chlorostyrene (4CLS) was purchased from Tokyo Kasei Kogyo Co., and was purified by distillation under reduced pressure. Random copolymer poly(dimethylsiloxane-co-diphenylsiloxane) (PDMScoDPS) was a commercial product (Shin-Etsu Chemical Co., KF54) and was used as supplied. Its average molecular weight and molecular weight distribution were evaluated by size exclusion chromatography to be $M_w = 3.4 \times 10^3$ and $M_w/M_n = 1.13$ in equivalence to polystyrene standards. The content of diphenylsiloxane unit in the copolymer was determined by

^{1}H-NMR to be 27 mol %. After being filtrated with a Millipore filter of 3-μm pore size, PDMScoDPS was mixed with 4-chlorostyrene in a ratio of 1:1 by weight at room temperature. A sample mixture was placed on a slide glass with a 0.05-mm-thick spacer made of polytetrafluoroethylene and covered with a cover glass. Polymerization and phase separation were made on a hot stage Metler FP82. Polymerization was initiated by raising the temperature without the aid of an initiator. The morphological structure of phase-separated domain was observed with a phase contrast microscope and an ordinary optical microscope. Observations of domain structures with the phase contrast microscope were made for samples quenched to room temperature. Reaction conversion of 4CLS was determined with a size exclusion chromatography apparatus, Toso HLC803D, equipped with a differential refractometer as a detector. Conversion was calculated from an area ratio of two separate peaks, respectively, corresponding to poly(4-chlorostyrene) (P4CLS) produced by polymerization and PDMScoDPS, with the correction made for the difference in refractive index increment in an eluent.

Figure 1 shows morphological structures, observed with a phase contrast microscope, of mixtures quenched to room temperature after the mixtures were kept at temperature $T = 100\,^\circ$C for the indicated duration of time t. At $t = 4$ h, it was seen that a demixed phase formed spherical domains (droplets). It was noticeable that these droplets showed quite narrow size distribution compared with those generally observed in polymerization-induced phase separation [1,7]. At $t = 8$ h, there appeared regions in which droplets formed a regular array like a crystal. The droplet diameter was 5 ∼ 6 μm and roughly $1/10$ of sample thickness (50 μm). The regular array was observed from both the top and bottom sides of the sample, suggesting that the array extended three dimensionally in the sample. A similar array was also observed at an earlier time of $t = 6$ h (not shown here) although it was less distinctive. At $t = 12$ and 18 h, a highly ordered array was clearly observed. The structure over a wider spatial

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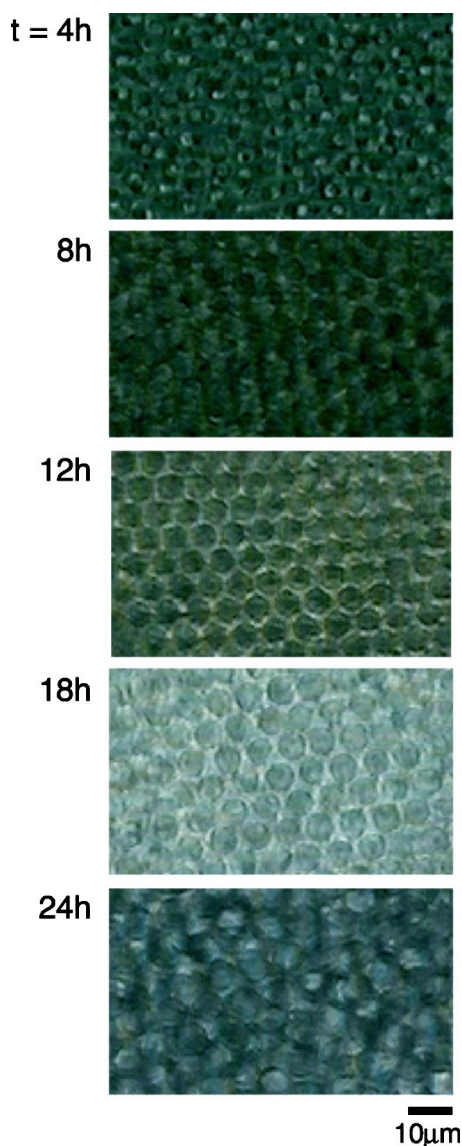*Electronic address: m.okada@iccas.ac.cn

FIG. 1. Phase-separated domain structures at temperature T =100 °C and time t, observed with a phase contrast microscope for samples quenched to room temperature. Initial monomer composition is 0.5 by weight.
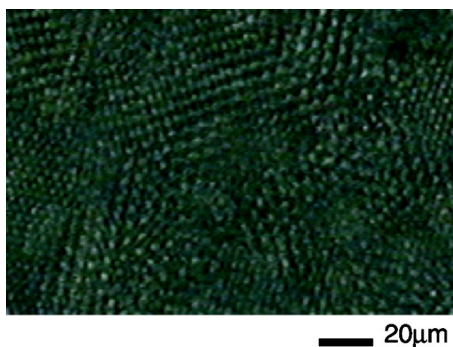

FIG. 2. Lower magnification image of phase-separated domains at temperature T=100 °C and time t=12 h.
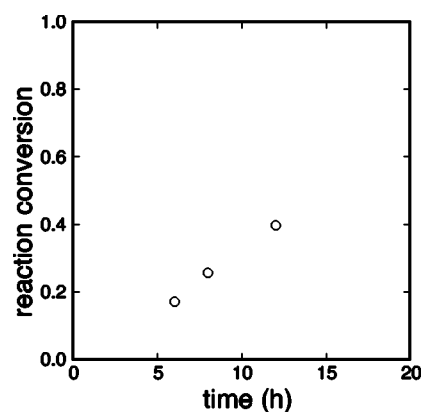

FIG. 3. Reaction conversion of 4-chlorostyrene monomer at 100 °C against reaction time.

range is displayed in Fig. 2. Many dislocation lines (planes) ran across the array, and respective regions bounded by dislocation lines were relatively small, indicating that a regular array started to form at various locations in the mixture. At t=24 h, the array was no longer observed, and the shape of each droplet appeared to be distorted from a sphere. It was seen that droplets continued growing in size over the observed period from 4 to 24 h.

The structures shown in Figs. 1 and 2 were observed for samples quenched to room temperature. The observation of structures was also made *in situ* by using an optical microscope, and it was confirmed that the regular array formed at 100 °C although the observed image was not so clear as shown in Fig. 1. Although the glass transition temperature T_g of PDMScoDPS was lower than room temperature, the regular array structure was found to be stable at room temperature for at least three weeks. Thus, structure change during our observation at room temperature was negligible.

Figure 3 shows reaction conversions of 4CLS monomer determined by size exclusion chromatography measurements. In chain polymerization, to which radical polymerization belongs, it is known that the average molecular weight of a reaction product does not usually change with conversion. In fact, it was found that molecular weights at three reaction times shown in the Fig. 3 were roughly identical ($\sim 2 \times 10^5$). Therefore, Fig. 3 also indicates the change of the product concentration with time. The conversion was still low when the regular array formed around t=6 h. Therefore droplets, which were considered to correspond to the P4CLS-rich phase, as would be discussed later, consisted of viscous fluid rather than of amorphous solid (T_g of P4CLS is about 130 °C), at least at the point of time the array formed.

When polystyrene (PS) was used as a nonreactive component instead of PDMScoDPS, droplets also formed during phase separation induced by polymerization of 4CLS monomer, but the size distribution of droplets was much wider than in the present system, and no regular array formed [8]. A conspicuous difference between PDMScoDPS and PS lay in their viscoelasticity. PDMScoDPS had a much lower viscoelasticity than either PS or the reaction product P4CLS at the experimental temperature. Consequently, there was a large difference in the viscoelastic property between two segregating components, namely, P4CLS and PDMScoDPS, in

the present system. The difference in viscoelasticity or asymmetry of viscoelasticity between components is known to have significant effects on dynamics of thermoinduced phase separation [9–13], and a system consisting of components having largely different viscoelastic properties is described by a dynamic model different from model *B* and model *H* classified by Hohenberg and Halperin [14]. It was conceivable that asymmetry in viscoelasticity had noticeable effects on polymerization-induced phase separation (PIPS) as well.

It has been reported that droplets with narrow size distribution appear in a mixture of asymmetric viscoelastic components when a deep quench is made at an off-critical composition on the low viscoelastic component-rich side of the phase diagram [9]. The narrow distribution of droplet size is speculated to reflect a distribution of concentration fluctuation wavelength in the spinodal decomposition that precedes the formation of droplets. Droplets move rapidly and collide with each other, but coalescence of droplets hardly occurs ("moving droplet phase"). The suppression of coalescence results from the fact that the characteristic time of collision between two droplets (contact time) is much shorter than the characteristic rheological time of the higher viscoelastic phase. Diffusion of polymer chains through the contact surface is necessary for two droplets to coalesce, and consequently the dynamics of coalescence depends greatly on the viscoelastic properties of the droplet phase, while the time span during which two droplets are in contact depends rather 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 becomes much longer than the contact time.

In phase separation induced by radical polymerization of a monomer in the presence of a different polymer, the phase being rich in the product of polymerization reaction generally forms droplets [7,15]. In fact, polymerization of 4CLS in the presence of PS generated droplets of the P4CLS-rich phase over a wide range of initial monomer concentration and temperature [8]. Thus it was reasonable to consider that droplets observed in the present system corresponded to the P4CLS-rich phase. The P4CLS-rich droplets had a higher viscoelasicity than the surrounding PDMScoDPS-rich phase and were expected to hardly coalesce by collisions as in the

"moving droplet phase." However, it was not clear why droplets with a narrow size distribution appeared in PIPS. As mentioned above, it has been speculated that the uniform droplet size in viscoelastic phase separation is caused by spinodal decomposition in the earlier period. This explanation did not apply to the case of PIPS, where the system went through the metastable region before it reached the unstable region, unless the nucleation and growth were extremely slow compared with polymerization reaction. Each droplet probably grew by absorption of monomers and adsorption of isolated P4CLS chains on the surface, because coalescence of droplets did not occur. Thus, when only a single size of droplets existed initially, the size distribution was expected not to be broadened so much.

Since there did not seem to exist strong attractive interaction between droplets, a conceivable origin of the regular array formation was the Alder transition [16,17]. It is known that hard spheres of uniform size undergo a fluid-to-solid phase transition as their density increases. The transition was initially observed for a one-component liquid and was found later for a polymer latex solution [18]. Since viscoelastic droplets were similar to polymer latexes in the sense that they do not coalesce by collisions, the same mechanism as the Alder transition was expected to work in PIPS. The difference was in the way the particle density changed. The transition was caused by an increase in the number of particles in the case of hard sphere and polymer latex, while it was caused by an increase in the volume of each droplet associated with proceeding of polymerization reaction in PIPS. This also explained the later change of the structure. When droplets continued to grow and their size exceeded the close-packed volume, the droplets would be deformed and eventually the array structure would be destroyed since droplets were not real hard spheres.

The present work showed that PIPS of a rather simple fluid mixture produced a highly regular structure. We speculated the physical origin of the regular pattern formation on the basis of asymmetry of viscoelastic properties between segregating components, but several points remained unexplained. Elucidation of this unique phenomenon is considered to be of fundamental importance in understanding pattern formation in PIPS.

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