

## Hexagonal phase induced by a reversible photo-cross-link reaction in a polymer mixture

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(Received 24 April 2007; published 13 February 2008)

A hexagonal phase was found during the synthesis of interpenetrating polymer networks composed of polystyrene (PS) and poly(methyl methacrylate) (PMMA). By using confocal microscopy, it was found that the regularity of this hexagonal phase further increases upon de-cross-linking of the PS networks in the matrix phase by irradiation with shorter uv wavelengths. We conclude that the cooperation between the cross-link-induced suppression of phase separation and the elastic repulsion between the dispersed PMMA-rich domains is responsible for the emergence of this hexagonal phase.

DOI: [10.1103/PhysRevE.77.020801](https://doi.org/10.1103/PhysRevE.77.020801)

PACS number(s): 82.35.-x, 64.75.-g, 05.65.+b, 89.75.Fb

Phase separation of polymer mixtures induced by a chemical reaction is a typical behavior of systems with competing interactions under some specific conditions such as cross linking [1]. In these particular cases, the cross-linking reaction between polymer chains thermodynamically destabilizes the mixture, inducing phase separation, whereas the networks generated by the reaction tend to sustain their miscibility. The analogy between polymers with competing interactions and small-molecule systems exhibiting Turing structure derived from the “activator-inhibitor” interactions [2] is much more obvious for the case of microphase separation of block copolymers. Here two or more immiscible polymer components with monodisperse chain lengths are covalently linked together, forcing these incompatible components to stay together within the radius of gyration of the molecule [3]. For nonpolymeric mixtures, it has been theoretically predicted that under some particular conditions a reversible reaction can suppress concentration fluctuations with long wavelengths, leading to self-ordering phenomena [4,5]. For reacting polymer mixtures, the situation is more complicated due to the emergence of viscoelasticity, an inherent property of chain-molecule systems [6]. Theoretically, it was predicted that the coupling between the critical fluctuations and the elastic stress acting as a long-range effect could lead to some unique mode selection in the resulting morphologies [7]. Significant effects of these long-range interactions on the phase separation of polymeric systems have been experimentally verified for polymer blends cross linked by periodic uv irradiation [8].

In general, the principal patterns emerging from systems with competing interaction are either stripes or hexagons. Experimentally, we have demonstrated that the modes with long wavelengths that correspond to large structures can be suppressed by using appropriate photochemical reactions, resulting in modulated and lamellar structures [9]. In order to verify that the hexagonal structure is one of the general features of polymeric systems with competing interactions, we have designed a reacting polymer mixture with viscoelastic properties controllable by light. The formation of polymer networks in these mixtures can be reversibly controlled by

irradiation with two different ultraviolet wavelengths [10], so that the viscosity of the matrix phase as well as the elastic repulsion between the dispersed domains can be adjusted by uv irradiation.

In this Rapid Communication, by experimentally introducing a cutoff into the long-wavelength side of the concentration fluctuations and simultaneously controlling the elastic repulsion between phase-separated domains by using a reversible photo-cross-link reaction of anthracene, we are able to show that the hexagonal phase can emerge in reaction-induced phase separation of polymer blends.

Samples used in this work are mixtures of polystyrene doubly labeled with anthracene and fluorescein (PSAF) dissolved in distilled methyl methacrylate (MMA) monomer containing ethyleneglycol dimethacrylate (EGDMA) as a cross linker and 2,4,6-trimethylbenzoyl diphenylphosphine (Lucirin TPO) as a photoinitiator for the MMA monomer, as reported previously [11]. The concentration of EGDMA and Lucirin TPO was kept, respectively, at 2 and 4 wt % with respect to the total weight of MMA. The composition of all the PSAF-MMA mixtures was fixed at 5:95. By irradiation with uv light (365 nm, 0.01 mW/cm<sup>2</sup>), the PSAF component is cross linked due to the photodimerization of anthracene labeled on the PSAF chains, whereas the MMA monomer is simultaneously polymerized and cross linked in the presence of ethyleneglycol dimethacrylate. By this procedure, two independent nonintersecting networks of PSAF and poly-MMA (PMMA) can be generated and controlled by irradiation. The experimental temperature was kept at 30 °C.

The demixing process of a homogeneous mixture upon irradiation was observed *in situ* under a laser scanning confocal microscope (LSCM) (LSM 5 Pascal, Carl Zeiss). The details of the experimental procedure as well as data analysis were provided elsewhere [11]. The irradiation time  $t_0$  required for the onset of phase separation was found to be 600 s as determined from the sudden change in the integrated fluorescence intensity under the experimental conditions. Figures 1 show an overview of the phase-separation process observed for a PSAF-MMA (5:95) mixture irradiated at 30 °C. Figure 1(a) displays the fluorescence micrographs observed by the LSCM with the dimension  $230.3 \times 230.3 \mu\text{m}^2$  taken at approximately  $12.5 \mu\text{m}$  from the surface. The green (bright) region in the micrographs represents the PSAF-rich phase as imaged by the fluorescence of fluorescein, whereas the nonfluorescent black domains corre-

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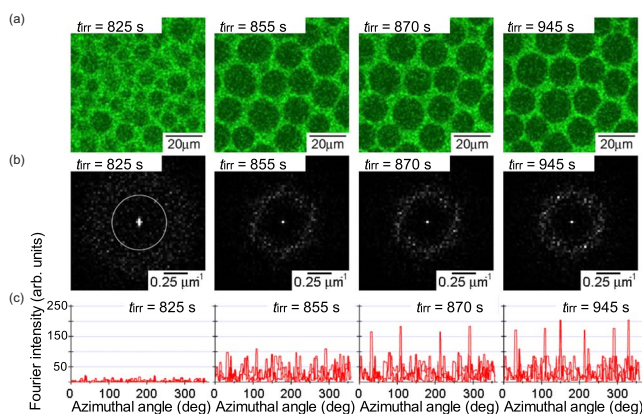


FIG. 1. (Color online) Time evolution of the morphology observed under various irradiation times ( $t_{irr}$ ) using 365 nm uv light. (a) LSCM images taken at approximately  $12.5 \mu\text{m}$  from the surface; (b) the corresponding 2D FFT power spectra; (c) azimuthal distribution of the 1D Fourier intensity corresponding to the circle drawn in (b).

spond to the PMMA-rich phase. The corresponding two-dimensional (2D) fast Fourier transform (FFT) power spectrum and the 1D azimuthal distribution of the Fourier intensity obtained at  $q=0.31 \mu\text{m}^{-1}$  are illustrated, respectively, in Figs. 1(b) and 1(c) as a function of irradiation time  $t_{irr}$ . Small irregular droplets developing from the spinodal decomposition mechanism grow quickly with irradiation time and become almost unchanged with irradiation time after 870 s of irradiation. At this stage, though considerably frozen by the cross-link reaction, these droplets slowly rearrange themselves into hexagonal packing as revealed by the sharp peaks appearing in the azimuthal distribution of the Fourier intensity shown in Fig. 1(c). The regularity of this hexagonal packing becomes more significant as irradiation time increases from 870 to 945 s, and eventually six sharp peaks clearly appear in the azimuthal intensity distribution, reflecting a well-packed hexagonal structure. It is worth noting that, as the equilibrium sizes of the PMMA-rich domains approach the sample thickness, a hexagonal phase with high regularity is obtained, whereas this regularity is lower when the final size of the PMMA-rich domains is less than the sample thickness. Furthermore, this regularity is high in the vicinity of the interface between the sample and the two cover slips, but becomes less regular in the center of the sample.

To gain some insight into the mechanism of this cross-link-induced hexagonal packing, the polymerization yield  $\Phi$  of MMA monomer was measured *in situ* during the irradiation process by using FTIR spectroscopy [11]. As shown in Fig. 2, the yield  $\Phi$  of polymerization and cross-link reaction exhibits a sigmoidal dependence on the irradiation time  $t_{irr}$ , suggesting that the polymerization process of MMA was promoted in an autocatalytic fashion, i.e., the so-called Trommsdorff effect [12]. The mean reaction rate defined as  $d\Phi/dt_{irr}$  is shown as a solid curve with a maximum at  $t_{irr}=1480$  s that corresponds to the inflection point of the  $\Phi$  vs  $t_{irr}$  curve. On the other hand, the kinetics of phase separation was investigated by following the time evolution of the number-average

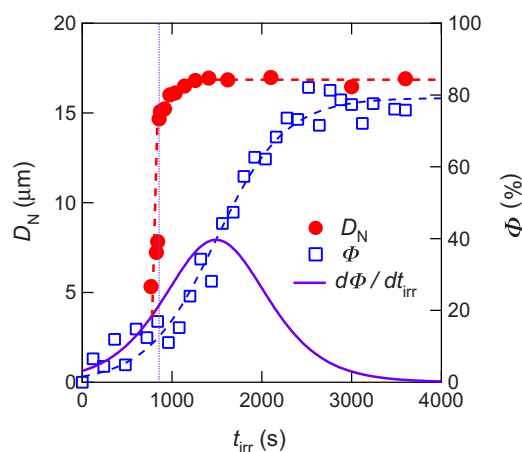


FIG. 2. (Color online) Irradiation-time dependence of the polymerization yield  $\Phi$  and the average diameter  $D_N$  of the PMMA-rich droplets. The vertical dotted line corresponds to the irradiation time  $t_{irr}=855$  s.

diameter  $D_N$  of these droplets defined as  $D_N = \sum_i D_i f(D_i)$ . Here  $D_i$  is the diameter of the  $i$ th droplet measured by digital image analysis and  $f(D_i)$  is the discrete probability distribution function of the diameter  $D$ . The average was taken over a large number (200–300) of droplets in the morphology. As illustrated by the dotted line in Fig. 2, the number-average diameter  $D_N$  steeply increases with irradiation time in the vicinity of 855 s and eventually reaches a stationary state at long time. The irradiation time  $t_{irr}$  at which the droplet size  $D_N$  reaches the stationary state corresponds well to the time  $t_{max}$  where the rate of polymerization  $d\Phi/dt_{irr}$  reaches its maximum. It should be noted that, for  $t_{irr}=855$  s, a large amount (ca. 90%) of unreacted MMA monomer still remains in the mixture, implying that the mixture was not yet vitrified at this stage of irradiation. Indeed, *in situ* observation under the laser confocal microscope reveals that the PMMA-rich droplets no longer coalesce although they continue changing their local arrangements even after  $t_{irr}=855$  s. These results suggest the active role of the elastic repulsion exerted among these PMMA-rich droplets at this stage of phase separation.

The three-dimensional morphology obtained after 60 min of irradiation with 365 nm is displayed in Fig. 3, revealing clear evidence for the elastic repulsion between the PMMA-

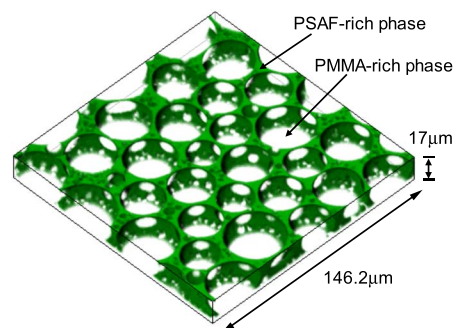


FIG. 3. (Color online) 3D stationary morphology generated by irradiation with 365 nm uv light over 60 min. Both the domains are continuous phases.

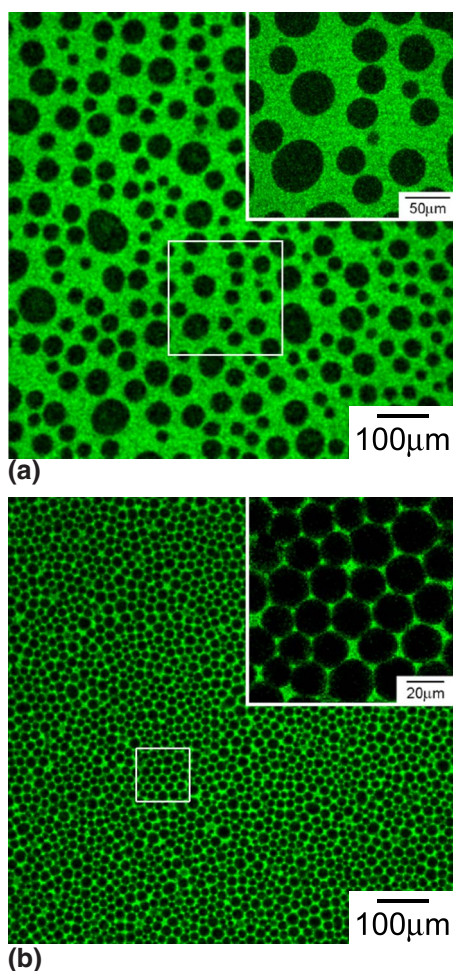


FIG. 4. (Color online) (a) Random two-phase structure emerging after quenching into the unstable region by irradiation with 365 nm light for 10 min and subsequently staying in the dark for 60 min. The structure inside the square is enlarged and illustrated in the inset. (b) Hexagonal phase induced by de-cross-linking the PSAF-rich (bright, green) matrix and simultaneously cross-linking the PMMA-rich (dark, black) droplets by irradiation with 297 nm light. The structure inside the square is enlarged and illustrated in the inset.

rich (transparent) droplets. Here, the transparent “windows” bridging the spherical PMMA-rich domains reveal the interconnectivity among these (transparent) spheres in the continuous phase of the PSAF matrix (bright green) at the late stage of phase separation. This unique hexagonal morphology is evidence for the inhibition of the mutual diffusion of PMMA chains among the PMMA droplets, except in some limited areas at the droplet-matrix interfaces that later appear as the transparent windows in the 3D morphology depicted in Fig. 3.

To verify the role of cross linking in the formation of this hexagonal phase, phase separation of a PSAF-MMA (5:95) mixture was first induced by irradiation with uv light (365 nm, 0.01 mW/cm<sup>2</sup>) over 10 min at 30 °C. Then the uv light was turned off and the reacted mixture was allowed to stay in the dark (without further cross linking) at the same temperature while the observation was continued under the

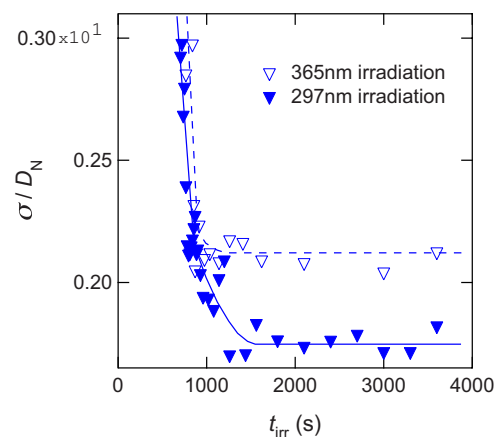


FIG. 5. (Color online) Irradiation-time dependence of the normalized diameter distribution  $\sigma/D_N$  of the PMMA-rich droplets obtained by cross linking with 365 nm light only for 60 min (dashed line); cross linking with 365 nm light for 10 min, and successively de-cross-linking with 297 nm light for 50 min (solid line).

LSCM. Figure 4(a) shows the morphology of the irradiated mixture obtained after it was maintained in the dark for 60 min. Under this particular condition, the size of these droplets continues increasing with irradiation time until the mixture reaches phase equilibrium with a random two-phase structure. It should be noted that the PSAF-rich (green, bright) domains in the morphology do not reflect the fraction of PSAF in the mixture because there still exists a large amount of unreacted MMA monomer in these PSAF-rich domains at the early stage of irradiation, as revealed by the reaction kinetics shown in Fig. 2. However, as polymerization of MMA proceeds, the fluorescing fraction in the morphology gradually decreases, reflecting the initial composition of the mixture.

The strong kinetic effect associated with the increase in viscosity of the mixtures can be minimized by de-cross-linking the PSAF networks, taking advantages of photodissociation of anthracene photodimers [13]. For this purpose, a PSAF-MMA (5:95) mixture was first irradiated with 365 nm. As soon as phase separation took place, the irradiation wavelength was instantaneously switched from 365 to 297 nm to induce photodissociation of anthracene photodimers (the cross-link points) in the PSAF-rich matrix and to increase, at the same time, the cross-link density in the PMMA-rich spherical domains by further excitation of the photoinitiator Lucirin TPO. The morphology obtained after 60 min of irradiation using these two uv wavelengths, i.e., promoting phase separation by 365 nm for 10 min and subsequently homogenizing the phase-separated blend using 297 nm for 50 min, is illustrated as an example in Fig. 4(b). It was found that hexagonal packing was sporadically generated in the reacting mixture as depicted in the inset of Fig. 4(b).

The evolution of this ordering phenomenon with irradiation time is depicted in Fig. 5, where the normalized diameter distribution  $\sigma/D_N$  of these PMMA droplets is plotted versus irradiation time for a mixture irradiated successively with 365 nm uv light (to promote phase separation) and 297 nm (to homogenize the mixture). Here,  $\sigma = \sqrt{\sum(D - D_N)^2 f(D)}$  represents the standard deviation of the



droplet diameter  $D$ .  $D_N$  and  $f(D)$  are, respectively, the number-average diameter and its distribution function. Compared to the forward process induced by irradiation with 365 nm only,  $\sigma/D_N$  decreases much faster upon de-cross-linking the PSAF network with 297 nm light. These results indicate that reducing the viscosity of the PSAF-rich matrix phase by irradiation with 297 nm light has further promoted the local adjustments of the PMMA-rich droplets in the matrix toward the hexagonal arrangements, revealing the existence of a free-energy minimum corresponding to the hexagonal phase. Thus, additional irradiation at 297 nm for 50 min has increased the mobility of the PSA-rich matrix phase and simultaneously enhanced the elastic repulsion between PMMA-rich droplets, leading to their hexagonal packing. It is worth noting that the hexagonal phase has been

found previously in several systems with competing interactions, such as polymer mixtures undergoing phase separation induced by free-radical polymerization [14], and polymer solutions containing surfactants under evaporation [15] or with specific interactions with substrates [16]. Such ordering phenomena were intensively studied by computer simulation a decade ago [17]. However, for reacting polymer systems, further examination is demanded to elucidate the roles played by the continuous feedback from the reactions on the viscoelasticity of the mixture.

We thank the Ministry of Education, Japan for the Grant-in-Aid No. 19031018 on the Priority Research Area No. 463 “Soft Matter Physics.” The assistance of Dr. Tomohisa Norisuye in data analysis is also acknowledged.

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