REVIEW

Design and morphology control of polymer nanocomposites using light-driven phase separation phenomena

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Abstract

Phase separation of polymer mixtures is induced and controlled by photo-cross-link and photopolymerization using ultraviolet (UV) light. By taking advantage of the competition between phase separation and chemical reactions, a variety of morphologies such as co-continuous, spatially graded co-continuous and periodic structures with controllable periods, and hexagonal structures, etc, are obtained experimentally. The reaction kinetics (photo-cross-link or photopolymerization), reaction-induced elastic strain and phase separation kinetics are monitored, respectively, by UV–Vis spectroscopy, FTIR, Mach–Zehnder interferometry (MZI), light scattering (LS) and laser-scanning confocal microscopy (LSCM). Spatial modulation of light intensity generated by computer-assisted irradiation (CAI) is also used to induce phase separation of polymer blends. The correlation between the reaction-induced phase separation of polymer mixtures and the competing interactions is discussed with some perspectives on designing polymer materials with high performance.

Keywords: polymer blends, photo-crosslink reaction, phase separation, nanocomposites, laser scanning confocal microscopy, Mach–Zehnder interferometry

Classification numbers: 5.00, 5.11

1. Introduction

Polymer alloys, i.e. mixtures of more than two kinds of polymer, have been a central research topic in the field of polymer materials science over the past half century owing to the demands of materials science \cite{1}. In most cases, blending different polymers leads to phase separation because of the small mixing entropy and the strong interactions between these polymer components. From the pioneering research on the phase separation kinetics of metallic alloys, it is known that, besides the conventional nucleation process, there exists a significant region inside the phase diagram where the concentration fluctuations become unstable to small perturbations and grow exponentially with time \cite{2}. The resulting periodic continuous morphology is important for both fundamental and applied research due to its three-dimensional connectivity which could render materials with great applicability such as improving the brittle-ductile transition \cite{3}, or increasing the conducting properties \cite{4}. Since morphologies resulting from the spinodal decomposition process are mutually interconnecting, the so-called bi-continuous structures, a large number of studies
on design and control of these structures in polymer materials have been carried out in polymer blends [5] and particularly in block copolymers [6–8]. From the viewpoint of pattern formation [9–11], these bi-continuous structures originate from the competition among interactions exerted antagonistically over different length scales. In general, periodic structures can be generated from the competition between short-range activation and long-range inhibition. This is the principle of chemical morphogenesis arising from the coupling between reaction and diffusion known as the reaction–diffusion mechanism, proposed in 1952 by Turing [12]. Without being aware of this Turing mechanism, polymer chemists synthesized a wide variety of monodisperse block copolymers which exhibit various ordered structures such as spherical domains, cylinders, gyroids and lamellar structures. Recently, similar ordered structures with different length scales have been also found in a number of physical as well as biological systems, revealing the universality of systems with competing interactions [13].

From the viewpoint of polymer materials science, morphology with structural period in the mesoscale is expected because the microphase separation of block copolymers provides other structures limited on the nanometer scale. This restriction originates from the molecular weight limit of the block copolymer, which cannot reach the micrometer scale due to the current limitations of polymerization techniques [14–16]. To design polymers with ordered structures in the micrometer range, we applied this competing interaction principle to critical phenomena of polymer mixtures. Phase separation of polymer mixtures is induced by irradiation with ultraviolet (UV) light and, at the same time, the reactions (photo-cross-link and photopolymerization) are suppressed by an increase in viscosity. This situation generates inside the reacting polymeric systems a competition between two principal antagonistic interactions: phase separation and vitrification. The former is induced by thermodynamic instability coming mainly from the decrease in the mixing entropy of the mixtures, whereas the latter originates from the increase in viscosity of the mixture due to polymerization or cross-link reaction. These chemical reactions often proceed non-uniformly because of the dynamic heterogeneity of the local environment, widely known as free-volume distribution [17–19]. This effect is more remarkable for multi-component polymer systems with strong spatial or dynamic asymmetries. As a consequence, the strain field induced by the chemical reaction can greatly modify the thermodynamic instabilities of the mixture, leading to some unusual morphologies for reacting polymer blends. Furthermore, ultraviolet (UV) or visible (Vis) light can be a useful tool to manipulate the competition between these two processes. For polymeric systems, an additional and unique process comes into play in this competition: the elasticity originating from the interconnectivity of the polymer (chain) molecules. To control this viscoelastic property of the system, a reversible cross-link reaction is introduced into the reacting mixtures. In this paper, we will summarize our achievements in utilizing the competing process to generate and manipulate the regular structures at the micrometer and sub-micrometer scales in polymer mixtures. The formation and relaxation kinetics of the reaction-induced elastic strain will also be described and discussed in conjunction with chemical reaction kinetics. The experimental results will be discussed in terms of triangular correlations among the reaction kinetics (at the Angstrom scale), the reaction-induced elastic deformation (at the sub-micrometer scale) and the phase separation kinetics (at the micrometer scale).

2. Experimental

2.1. Sample preparation

In order to describe the competition between photo-cross-link/photopolymerization and phase separation, two kinds of experiments were performed: in solution and in bulk. The solution was composed of poly(styrene) doubly labeled with anthracene and fluorescein (PSAF) dissolved in methyl methacrylate (MMA) monomer. Mixtures of poly(vinyl methyl ether) (PVME) and polystyrene labeled with a cinnamic acid derivative (PSC) were used as samples in this study. Additionally, mixtures of anthracene-labeled polystyrene (PSA) and poly(vinyl methyl ether) (PVME) were utilized to investigate the formation and relaxation kinetics of the reaction-induced elastic strain.

2.1.1. Polystyrene labeled with anthracene (PSA) and doubly labeled with anthracene and fluorescein (PSAF).

The chemical structures of the polymers used in this study are illustrated in figure 1. The PS component was labeled with anthracene as a photo-cross-linker or doubly labeled with anthracene as a photo-cross-linker and fluorescein as a fluorescent marker. Upon irradiation with UV 365 nm, the PSA or PSAF component was cross-linked by photodimerization of anthracene, producing PSA or PSAF networks [20, 21]. For the bulk system, PSA/PVME (20/80) blends with thickness of around 10 µm were prepared by the solvent casting using toluene as the solvent.

For the solution system, a homogenous mixture of PSAF and MMA was made to observe a wide variety of morphologies generated under different experimental conditions. In this system, as PSAF was cross-linked, MMA was polymerized by the photoinitiator Lucirin TPO and networked by the cross-linker ethylene glycol dimethyl acrylate (EGDMA). Eventually, two types of network, PSAF and PMMA, were produced in the mixture upon irradiation with 365 nm as schematically presented in scheme 1 [21]. As the reaction yield of the PSAF and PMMA components exceeded a critical threshold, phase separation took place, giving rise to various morphologies depending upon the competition between the photo-cross-link reactions (and photopolymerization) and phase separation between the PSAF and PMMA components. The products are full-interpenetrating polymer networks (IPNs) composed of polystyrene and poly (methyl methacrylate).

2.1.2. Polystyrene labeled with trans-cinnamic acid derivative (PSC).

To induce phase separation with visible light, the PS component was labeled with trans-cinnamic acid derivative (PSC) (figure 1(d)). A polymer blend with a
lower critical solution temperature (LCST) was made by mixing PSC with PVME. To carry out the cross-link reaction of PSC by photodimerization of trans-cinnamic derivative, 5-nitroacenaphthene (Tokyo Kasei Inc.) was added to the mixture as a photosensitizer with a concentration of 1.5% wt. Upon irradiation with 405 nm, the 5-nitroacenaphthene was excited and transferred its triplet excited energy to cinnamic acid labeled on the PS chains, triggering the photodimerization of cinnamic acid. As a result, the PSC component formed a network under irradiation with visible light.

The characteristics of polymers used in this study are summarized in table 1.

2.2. Characterization methods

2.2.1. Reaction kinetics of anthracene photodimerization with UV light monitored by UV–Vis spectrometry. The photodimerization of anthracene labeled on the PS chain was monitored by following the decrease in the absorption of anthracene OD(t) at 365 nm under irradiation using UV–Vis spectrometry (UV-1600, Shimadzu Inc., Japan). From the above result, the time-evolution of normalized OD (OD_N(t)) and cross-link density (γ(t)) was defined as

\[
OD_N(t) = \frac{OD(t)}{OD(0)},
\]

\[
γ(t) = \frac{δ (OD(0) − OD(t))}{OD(0)},
\]

where δ is the average number of anthracenes labeled per PS chain. OD(0) and OD(t) are, respectively, the absorbance of anthracene at irradiation time t = 0 and t = t.

2.2.2. Upon irradiation with 365 nm, reaction kinetics of MMA photopolymerization monitored by FT-IR. The polymerization of MMA was monitored by following the decrease in the absorption of the C=O stretching mode (1640 cm⁻¹) of the MMA monomer by FT-IR (Perkin-Elmer, Model Spectrum GX) with resolution 4 cm⁻¹. The absorption of the C=O bonds at 1720 cm⁻¹ was used as an internal reference because it is not involved in the reaction. The
kinetics of the polymerization of MMA was evaluated using the reaction yield $\phi$ defined as

$$\phi(\%) = \left\{ \begin{array}{ll}
\frac{(A_{C=C})_t}{(A_{C=C})_{t=0}} \\
1 - \frac{(A_{C=O})_t}{(A_{C=O})_{t=0}}
\end{array} \right\} \times 100, \quad (3)
$$

where $A$ represents the absorbance of the corresponding vibrational modes observed by FT-IR spectra [22].

2.2.3. In situ measurement of deformation/elastic strain by a Mach–Zehnder interferometer (MZI). The reaction-induced elastic strain was measured *in situ* using a Mach–Zehnder interferometer equipped with a high-pressure mercury lamp.
Scheme 2. Continued.

(350 W, Moritex, Japan) (scheme 2(a)). The details of instrumentation, measurements and data analysis were reported elsewhere [23]. Briefly, the sample was divided into two parts: the irradiated part for the detection of the deformation and the masked part used as an internal reference. The irradiation process was performed in situ via an optical fiber and a removable reflecting mirror. The interference caused by the difference in the optical path length deference (OPLD) between the reference beam and the test beam in the MZI unit was detected by a CCD camera. There are two factors affecting the OPLD: changes in the thickness ($\Delta d$) and in the refractive index ($\Delta n$) of the polymer film caused by the photodimerization of anthracene. From measurements of refractive index using a Prism Coupler (Metricon, Model-2010), it was found that the change in the refractive index corresponding to the photodimerization is negligible. Therefore, under this experimental condition, the OPLD can be approximated as

$$\text{OPLD} \approx (n_s - 1) \Delta d$$

and

$$\Delta d = (d - d_0),$$

where $d_0$ and $d$ are, respectively, the thickness of the blend before and after the photo-cross-link reaction, and $n_s$ is the refractive index of the sample. The deformation (or the strain) $\varepsilon$, defined as ($\Delta d/d_0$) of the cross-linked blends, can be calculated from:

$$\varepsilon = \frac{\Delta d}{d_0} = \frac{\text{OPLD}}{(n_s - n_0) d_0} = \frac{\text{OPLD}}{(n_s - 1) d_0}.$$

2.2.4. Light scattering experiment. The light scattering profile was monitored in situ using a light scattering photometer (Dyna-3000, 632.8 nm, Otsuka Electronics,
Figure 2. (a) Photo-cross-link kinetics (normalized optical density and crosslink density) observed for PSA/PVME (30/70) blend irradiated with 2.0 mW cm⁻² UV light at room temperature; (b) photopolymerization and photo-cross-link kinetics of the PMMA component in a PSAF/MMA mixture at 25 °C.

Japan) equipped with a high-pressure Hg–Xe lamp (350 W, Moritex, Japan). As illustrated in scheme 2(b), the UV light was set perpendicularly to the sample surface which was placed horizontally in the heating block. The scattering profile was detected at scattering angles ranging from −20° to +20° using a two-dimensional high-sensitivity movable CCD camera (Princeton Instruments Inc.). The one-dimensional profile was obtained by circularly averaging the two-dimensional scattering intensity distribution. The characteristic length scales of the morphology were calculated via two methods. For periodic (spinodal) structures, ξ was calculated from the Bragg condition \( ξ = 2 \pi / q_{\text{max}} \), where \( q_{\text{max}} \) is the wavenumber corresponding to the scattering peak. For droplet, non-periodic structures, the average scales of the morphology were calculated using image analysis software (ImageHyper2, Digimo Inc., Japan).

2.2.5. Morphology observation using a laser scanning confocal microscope (LSCM). The morphology was observed using a laser scanning confocal microscope (LSM 5 PASCAL, inverted type, Carl Zeiss) equipped with an Ar⁺ ion laser (488 nm) used to excite fluorescein on the PSAF component. Illustrated in figure 2(c) is the confocal system. The light emitted from out-of-focus regions was eliminated by the pinhole aperture attached in front of the detector. By collecting a series of thin optical sections through the thickness of the specimen, the three-dimensional morphology of the IPNs was reconstructed using the software Image Visart (v. 2.08, Carl Zeiss) and IMARIS (Bitplane Scientific Solutions Inc., V.6.1.0) for 3D construction. Several objective lenses with magnifications (×10: N.A. = 0.45, ×20: N.A. = 0.5, ×40: N.A. = 0.75, ×63 oil-immersion: N.A. = 1.4) were used for observation. All micrographs were taken at 512 × 512 pixels with 8 bit grayscale (256 levels). The resolution was adjusted to be same in all directions.

2.2.6. Generating and controlling the morphologies by computer-assisted irradiation (CAI). A computer-assisted irradiation (CAI) apparatus was designed to produce morphologies with arbitrary distribution of characteristic length scales. This allowed us to induce phase separation of a photosensitive polymer mixture by irradiation using a light pattern with arbitrary spatial and temporal distributions [24]. In this method, a pattern with a well-defined characteristic length scale \( ξ \) and characteristic time scale \( τ \) was first generated on a computer. This pattern was transferred to a digital projector and subsequently projected, as a visible light pattern, onto a photoreactive sample through a set of optical lenses. The resolution of this light pattern depends on the set of lenses and can be reduced down to 20 μm. For this CAI method, we also developed a series of polymer mixtures with phase separation inducible by visible light irradiation.

3. Results and discussion

3.1. Inhomogeneous kinetics of photo-cross-link reaction in the one-phase region

Figure 2(a) shows the time evolution of the normalized optical density \( OD_N(t) \) and cross-link density \( γ(t) \) calculated respectively by equations (1) and (2). It was found that both \( OD_N(t) \) and \( γ(t) \) can be well described by the following modified Kohlraush–Williams–Watts (KWW) stretched exponential [25, 26]:

\[
OD_N(t) = (1 - B) \exp[-(k_c t)^\alpha] + B, \tag{7}
\]

\[
γ(t) = D[1 - \exp(-(k_c t)^\alpha)], \tag{8}
\]

where \( k_c \) and \( β \) are, respectively, the mean reaction rate and the inhomogeneity index of the cross-link process, and \( B \) and \( D \) are, respectively, the limiting normalized optical density and the limiting cross-link density. These results reflect the inhomogeneous ongoing vitrification process in the photo-cross-linked polymer blend system. The behavior of the elastic strain induced by this cross-link process will be described and discussed later using the data obtained by MZI.

3.2. Cross-link kinetics of polymers in the mixture

It was found from the data shown in figure 2(b) that the networking kinetics exhibits an autocatalytic behavior, suggesting the role of heat of polymerization in both photo-cross-link and photopolymerization of MMA. This
reaction kinetics can be analyzed by fitting the data to an appropriate model of autocatalytic reaction [27]. In fact, this particular autocatalytic behavior of the reaction strongly affected the phase separation kinetics as described below. On the other hand, although the cross-link reaction of the PSAF component can be monitored by following the change in the absorption of the anthracene component, the cross-link kinetics of the PSA component could not be exactly observed because of the spectral overlap between the photoinitiator Lucirin TPO and anthracene. Nevertheless, correction for the contribution of Lucirin TPO to the absorbance in the vicinity of 365 nm, where the absorption of anthracene is significant, reveals the non-mean-field kinetics of the photodimerization of anthracene, i.e. the cross-link kinetics of the PSAF in the mixture proceeds inhomogeneously upon irradiation.

3.3. Elastic strain and its relaxation behavior observed by MZI

A PSA/PVME (30/70) blend was irradiated with 365 nm UV light over 210 min to observe the elastic strain generated by the photo-cross-link reaction. Here, the elastic strain $\varepsilon$ is defined as

$$\varepsilon = \frac{\Delta d}{d_0}. \quad \text{(9)}$$

For a constant irradiation intensity of 2.0 mW cm$^{-2}$, it was found that the elastic strain increased with the irradiation time, namely the sample shrank with the cross-link time (figure 3(a)). The time evolution of the elastic strain can be well expressed following the modified KWW stretched exponential:

$$\varepsilon (t) = E[1 - \exp (k_d t)^\beta], \quad \text{(10)}$$

where $k_d$ and $\beta$ are, respectively, the mean deformation rate and the inhomogeneity index of the shrinking process and $t$ is the irradiation time.

The correlation between the photo-cross-link reaction expressed by the cross-link density $\xi$ and its induced elastic strain $\varepsilon$ is shown in figure 3(b). It was found that as the cross-link density of the blend system increased, the sample deformed inhomogeneously. The relaxation behavior of the elastic strain was also observed after irradiating the system over different time intervals. Depending on the state of the cross-linked system with respect to the distance between the experimental temperature and the glass transition temperature ($T_g$), the cross-linked polymer may swell, persist or continue to shrink [28]. The relaxation behavior may explain the unusual dependence of the phase separation of the same mixture obtained by light scattering measurements.

3.4. Light scattering data of photo-cross-linked blends

Figure 4 shows the one-dimensional light scattering profile obtained after circularly averaging the two-dimensional data for a PSA/PVME (20/80) blend cross-linked under 365 nm UV light at 110 °C with $I = 0.2 \text{ mW cm}^{-2}$ [29]. The shift of the scattering peak toward larger wavenumber $q$ is distinctly opposite to the normal behavior of phase separation which has been observed for non-reacting mixtures. The phase separation kinetics of the reacting systems is more complicated due to the mutual coupling among the nonlinear kinetics of the evolving reactions, the reaction-induced fluctuations, the polymer viscoelasticity, and the change in the compressibility of the systems during the course of the reaction. To confirm that the volume of the cross-linked blend may be changed upon irradiation, a Mach–Zehnder interferometer was employed to monitor in situ the local deformation of the blend during irradiation. The rate of shrinkage $k_d$ measured by MZI and the shifting rate of the scattering peak $k_\xi$ exhibit strong correlation. The shifting rate $k_\xi$ increases with the $k_d$ of the cross-linked blend. These results lead to the conclusion that the shrinkage of the blend over the course of the reaction is responsible for the shift of the scattering peaks toward larger wavenumber $q$.

3.5. Several examples of competing interactions in reacting polymer mixtures

As mentioned previously, by coupling photochemical reactions to phase separation of polymer mixtures, a wide
variety of morphologies can be generated and manipulated by irradiation with UV light. These structures were generated by the competition between two antagonistic interactions: photo-cross-link/photopolymerization and phase separation. As a consequence of these competition processes, a variety of regular structures such as co-continuous periodic [30], hierarchical [31], periodic morphology with arbitrary length scales distribution [24], spatially gradient [32] and hexagonal [33]. These morphologies were observed in situ under an LSCM (Zeiss Inc., Pascal LSM-5) and analyzed by either digital image analysis or 2D Fourier transform.

3.5.1. Polymers with bi-continuous structure at the micrometer scale. Upon irradiation with 365 nm UV light, anthracene labeled on the polystyrene derivative PSAF undergoes photodimerization, leading to the formation of PSAF networks in the mixture. The same 365 nm UV light triggers photopolymerization of methyl methacrylate (MMA) initiated by Lucirin TPO and the photo-cross-link reaction of MMA due to EGDMA. As the fraction of PMMA networks and PSAF exceeds a threshold, phase separation takes place, but the viscosity of the irradiated mixture continues to increase until the whole system becomes glassified. The resulting morphology is determined by these two factors: the development of the continuous periodic morphology driven by thermodynamic instability and the suppression arising from the increase in viscosity induced by polymerization and cross-link. An example is illustrated in figure 5 where the bi-continuous periodic structures of polystyrene (green imaged by fluorescence) and of poly(methyl methacrylate) (black, non-fluorescent) were observed and imaged under an LSCM. Depending upon the strength of these competing processes, the resulting morphology can vary from bi-continuous, periodic, random two-phase structures to hierarchical morphologies. Varying the light intensity is one way of changing the magnitude of these competitions and thereby switching the morphology from one to the other.

3.5.2. Polymers with hierarchical morphology prepared by irradiation with UV light. As a general principle, hierarchical structure is a consequence of the co-operation and competition among non-uniform kinetic processes taking place over a long time in a system. Typical hierarchical structures have been seen in Nature where all the dynamic processes proceed over a very long time in non-uniform ways. For phase separation induced by photochemical reactions, similar processes can be induced by manipulating the irradiation process. Here, we demonstrate that by manipulating photodimerization of anthracene as a photo-cross-link reaction for polymer, a variety of hierarchical morphologies can be generated. It was found that when a mixture of PSAF/MMA (5/95) was irradiated with 365 nm light, the PSAF component forms a network. The PMMA networks were simultaneously generated in the mixture using Lucirin TPO as a photoinitiator and ethylene glycol dimethacrylate (EGDMA) as a cross-linker. First, irradiating the mixture with UV light at room temperature for 10 min resulted in a two-phase bi-continuous structure with PMMA-rich phase dispersed in a matrix of PSAF-rich phase. The mixture was then allowed to stay at the experimental temperature for 60 min in the dark and was subsequently irradiated over 50 more minutes with 365 nm UV light with an intensity three times stronger than the initial irradiation. It was found that inside the PSAF-rich phase, the secondary spinodal decomposition process took place, giving interconnecting domains within the PSAF-continuous structure.
phases. The characteristic length scale resulting from the primary phase separation is about one order of magnitude larger compared to those of the secondary phase separation. These two distributions could be observed by light intensity and irradiation time.

3.5.3. Polymers with spatially graded morphology induced by a strong light intensity. It is well known that light propagating inside a given medium is attenuated by absorption. Moderate intensity of incident light will follow the Lambert–Beer law and exponentially decay with propagation distance inside the sample. On the other hand, the significance of reaction-induced phase separation is that the mixture undergoes phase separation as soon as the reaction yield exceeds a critical value \( \phi_c \). The gap \( \Delta \phi = (\phi - \phi_c) \) with \( \phi \geq \phi_c \) defines the quench depth that controls the phase separation kinetics and the resulting morphology. Here, using strong UV light, we could produce a gradient of quench depth inside the sample. As a consequence, morphologies with various spatial gradients of length scales can be generated. As an example, a PSAF/MMA (10/90) mixture generated a gradient of the quench depth \( \Delta \phi \) by inducing phase separation of polymer mixtures with a gradient of light intensity and obtained polymers with controllable gradient morphologies at the micrometer scale. Figure 6 shows the 3D morphology taken by an LSCM at several depths along the propagation direction of 365 nm UV light. At low intensity (0.01 mW cm\(^{-2}\)), the effect of the light gradient on morphology is negligible and the morphology is completely uniform along the propagating direction of the incident light. However, as the irradiation intensity increases to 0.03 mW cm\(^{-2}\), morphology with spatially graded length scales appears. This morphological gradient changes with the light intensity and can be approximated by a power law with respect to the sample thickness [32]. Illustrated in figure 6 is the 3D morphology obtained by stacking a number of 2D morphologies observed with an LSCM.

3.5.4. Polymers with co-continuous structures with controllable characteristic length scales. However, this method is limited by the Lambert–Beer law which controls the gradient of the light intensity propagating inside the sample. In order to produce polymer materials with an arbitrary distribution of characteristic length scales, we have developed the so-called CAI method. This allows us to induce phase separation of a photosensitive polymer mixture by irradiation using a light pattern with an arbitrary distribution of characteristic length scales and arbitrary characteristic time scales [24]. In this method, a pattern with a well-defined characteristic length scale \( \xi \) and characteristic time scale \( \tau \) was first generated on a computer. This visible light pattern was transferred to a digital projector and subsequently projected onto a photoreactive sample through a set of optical lenses. The resolution of this light pattern depends on the set of lenses and can be reduced down to 20 \( \mu \)m. For this CAI method, we have also developed a series of polymer mixtures with phase separation inducible by visible light. An example is shown in figure 7 where a mixture of poly(vinyl methyl ether) (PVME) and polystyrene labeled with a cinnamic acid derivative (PSC) was irradiated with 405 nm light from a projector. The light pattern was designed on a computer as shown in the left inset of the figure. The intensity in these regions is 0.01 mW cm\(^{-2}\) for areas (A) and (C), and 1.0 mW cm\(^{-2}\) in the central part with the width \( L = 150 \mu \)m. The morphology obtained after 240 min of irradiation at 127 \( ^\circ \)C is illustrated in figure 7 where the mixture is still miscible in areas (A) and (C), while the periodic (spinodal) structures have already been developed in area (B) of the sample. By changing the light intensity distribution in these three areas, polymer blends with an adjustable distribution of periodic structures were obtained. Interestingly, the morphology in the vicinity of the boundary between areas with different periodic structures exhibits anisotropy, revealing the effects of phase separation with different quench depth. These results indicate that using this CAI method, not only can phase separation in the restricted dimension be studied, but the formation kinetics and morphology of polymer blends with controllable hierarchical structures are also examinable. These results may open a new route to studying critical phenomena permanently out of equilibrium or under restricted dimensions, polymer materials with a tailor-made arbitrary morphology distribution, and manipulation of the physical properties of multi-phase polymer materials.

3.5.5. Disorder–order transition in morphology of photo-cross-linked polymer mixtures: effects of elastic repulsion on the resulting morphology. Upon irradiation with 365 nm light, a PSAF/MMA (5/95) mixture undergoes phase separation via the spinodal decomposition and subsequently proceeds to a nucleation-and-growth process. At this stage, if the phase separation overcomes the polymerization and cross-link processes, the resulting morphology is a random two-phase structure as illustrated in figure 8(a). Here, the mixture was irradiated with 365 nm for 10 min to reach the two-phase region. Subsequently, the UV light was turned off and the irradiated mixture was allowed to stay in the dark for 60 min. After 10 min of irradiation, instead of keeping the mixture in the dark after cross-link, the UV light was switched from 365 nm to 297 nm to partially decross-link the PSAF networks and to initiate the formation of the PMMA networks in the reacting mixtures. As shown in figure 8(b), the irregular droplet morphologies become

Figure 6. Three-dimensional graded bi-continuous structure of a PSAF/MMA (10/90) mixture irradiated with 365 nm UV light from above. Green: PSAF-rich phase; transparent: PMMA-rich phase.
Figure 7. Upper part: the irradiation intensity profile (left) and morphology observed at low magnification. Lower part: enlarged morphology observed for different sections of the blend with the corresponding 2D FFT power spectra.

(a) Random two-phase structure obtained by irradiation over 10 min and subsequently keeping the sample in the dark for 60 min; (b) hexagonal morphology obtained with the same sample after irradiation with 365 nm in 10 min and switching the excitation wavelength to 297 nm. The experimental temperature is 25 °C.

well-packed hexagonal structures. The morphology inside the square in the center is enlarged and displayed in the upper-right inset of each figure. Further experiments suggest that there exists in the reacting polystyrene and poly(methyl methacrylate) a free-energy minimum corresponding to the hexagonal morphology.

4. Conclusions and perspective

By taking advantage of the competition between photochemical reactions and phase separation of polymer mixtures, we have demonstrated that it is possible to generate and control the length scales as well as the spatial distribution of morphologies in the micrometer range. In order to make use of these morphologies, we have introduced a start/stop interval into the irradiation process. The purpose is to manipulate the morphological regularity by introducing an annealing process into the phase separation to relax the elastic strain associated with the inhomogeneity of photochemical reactions in the bulk state of the polymers. This relaxation is very important for such control [34]. Experimentally, it has been shown that reversible cross-link reactions drivable by two UV wavelengths are useful for controlling the elastic strain associated with the cross-link reaction [29]. Furthermore, it has been shown that the relaxation process of the cross-link-induced elastic strain can be observed in situ by Mach–Zehnder interferometry during the cross-link process [23, 28].

Regarding the structure–property relationship of multiphase polymers, dynamic mechanical characterization of mixtures with the same composition, the same cross-link density but having different characteristic length scales shows
that the range of temperature where the peak of the loss tan δ appears, can be selected by controlling the regularity of the domain sizes. For a mixture with the same cross-link density, hexagonal morphology with higher regularity exhibits sharper distribution of tan δ, suggesting that it is a useful method of controlling the energy loss of the polymers [35]. These results may provide insight into the concept of mechanical bandgap polymers in comparison to their counterpart, photonic bandgap materials. Finally, by taking advantage of the generation of co-continuous morphologies by UV irradiation, percolating networks of the third additive component such as dendrimers or carbon nanotubes may be designed and manipulated to provide polymer materials with excellent mechanical and/or conducting performance.

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References

[1] Anraki T, Tran-Cong Q and Shibayama M (ed) 1998 Structure and Properties of Multiphase Polymeric Materials (New York: Marcel Dekker)
[2] Cahn J W and Hilliard J E 1958 J. Chem. Phys. 28 258
Cahn J W and Hilliard J E 1959 J. Chem. Phys. 31 688
Cahn J W 1961 Acta Metall. 9 795
Cahn J W 1962 Acta Metall. 10 179
[3] Wu S 1985 Polymer 26 1855
Wu S 1990 Polym. Eng. Sci. 30 753
[4] Stauffer D 1985 Introduction to Percolation Theory (London: Taylor and Francis)
[5] Paul D R and Bucknall C B 2000 Polymer Blends (New York: Wiley)
[6] Hadjichristidis N, Pispas S and Floudas G A 2003 Block Copolymer (Hoboken, NJ: Wiley-Interscience)
[7] Matushita Y 2007 Macromolecules 40 771
[8] Bates F S and Fredrickson G H 1990 Annu. Rev. Phys. Chem. 41 525
[9] Cross M C and Hohenberg P C 1993 Rev. Mod. Phys. 65 851
[10] Nicolis G and Prigogine I 1989 Exploring Complexity (San Francisco, CA: Freeman)
[11] Pojman J A and Tran-Cong-Miyata Q 2004 Nonlinear Dynamics in Polymeric Systems (ACS Symposium Series vol 768) (Washington, DC: American Chemical Society)
[12] Turing A 1952 Phil. Trans. R. Soc. B 237 37
[13] Seul M and Andelman D 1995 Science 267 476
[14] Matyjaszewski K 1996 Cationic Polymerizations—Mechanisms, Synthesis and Applications (New York: Marcel Dekker)
[15] Hsieh H and Quirk R Q 1996 Anionic Polymerization: Principle and Practical Applications (New York: Marcel Dekker)
[16] Matyjaszewski K 2000 Controlled/Living Radical Polymerization (ACS Symposium Series vol 768) (Washington, DC: American Chemical Society)
[17] Paik C S and Morawetz H 1972 Macromolecules 5 171
[18] Lamarre L and Sung C S P 1983 Macromolecules 16 1729
[19] Royal J S and Torkelson J M 1993 Macromolecules 26 5331
[20] Harada A and Tran-Cong Q 1997 Macromolecules 30 1643
[21] Nakanishi H, Satoh M, Norisuye T and Tran-Cong-Miyata Q 2004 Macromolecules 37 8495
[22] Ryan M E and Dutta A 1979 Polymer 20 203
[23] Inoue K, Komatsu S, Trinh X-A, Norisuye T and Tran-Cong-Miyata Q 2005 J. Polym. Sci. B: Polym. Phys. 43 2898
[24] Ishino S, Nakanishi H, Norisuye T, Awatsuji Y and Tran-Cong-Miyata Q 2006 Macromol. Rapid Commun. 27 758
[25] Williams G and Watts D C 1971 Trans. Faraday Soc. 66 80
[26] Kataoka K, Harada A, Tamai T and Tran-Cong Q 1998 J. Polym. Sci. Polym. Phys. 36 455
[27] Nakanishi H, Satoh M, Norisuye T and Tran-Cong-Miyata Q 2006 Macromolecules 39 9456
[28] Van Pham D-T, Sorioka K, Norisuye T and Tran-Cong-Miyata Q 2009 Polymer J. 41 260
[29] Trinh X-A, Fukuda J, Adachi Y, Nakanishi H, Norisuye T and Tran-Cong-Miyata Q 2007 Macromolecules 40 5566
[30] Tran-Cong Q, Kawai J and Endoh K 1999 Chaos 9 298
[31] Nakanishi H 2007 Generation and manipulation of ordered structures in interpenetrating polymer networks by using photochemical reactions PhD Dissertation Department of Macromolecular Science and Engineering, Kyoto Institute of Technology
[32] Nakanishi H, Namikawa N, Norisuye T and Tran-Cong-Miyata Q 2006 Soft Matter 2 149
[33] Nakanishi H, Sato M and Tran-Cong-Miyata Q 2008 Phys. Rev. E 77 020801
[34] Tran-Cong-Miyata Q, Nishigami S, Ito T, Komatsu S and Norisuye T 2004 Nat. Mater. 3 448
[35] Murata K, Murata T, Nakanishi H, Norisuye T and Tran-Cong-Miyata Q 2009 Macromol. Mater. Eng. 294 163