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Polymer Networks with Bi-continuous Gradient Morphologies Resulting from the Competition between Phase Separation and Photopolymerization

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Abstract

Poly(ethyl acrylate)/poly(methyl methacrylate) (PEA/PMMA) polymer networks (IPNs) with spatially graded bi-continuous morphology were designed and controlled by taking advantages of the spinodal decomposition process induced by photopolymerization of MMA monomer. Spatial gradients of the quench depth induced by the gradients of light intensity were generated along the path of the excitation light travelling through the mixture. Bi-continuous structures with uniaxial gradient of characteristic length scales were obtained by two different methods: simply irradiating the mixture with strong light intensity along the Z-direction, and using the so-called computer-assisted irradiation (CAI) method with moderate intensity to generate the light intensity gradient exclusively in the XY plane. These experimental results suggest that combination of these two irradiation methods could provide polymer materials having bi-axially co-continuous gradient morphology. An analysis method using the concept of spatial correlation function was developed to analyze the time-evolution of these graded The experimental results obtained in this study suggest a structures. promising method to design gradient polymers in the bulk state (3D) as well as on the surface (2D) by taking advantage of photo-polymerization.

Introduction

Spatially graded structures are ubiquitous in *Nature* where most of the kinetic processes are spatially and temporally non-uniform because these changes are continuously occurring over a very long period of time. The idea of fabricating gradient polymers was initiated from the "gradient polymer composites project" initiated by M. Shen and M.B. Bever in the US as early as in 1970's ¹. These projects aimed at fabricating polymer materials with physical (mechanical, optical, electrical etc.) responses which gradually change along a specific direction in the sample under consideration. Historically, several attempts to produce polymers with gradient structures have been made by diffusing a guest monomer into a host polymer followed by polymerization of the monomer present inside the host under a predetermined concentration gradient^{2, 3.} These fabrication techniques are mainly based on the synthesis method of interpenetrating polymer networks (IPNs)^{4,5} in which a spatial gradient of a polymer composition is generated from a composition gradient of the guest monomer undergoing polymerization inside the host. Since then, a number of experimental methods have been proposed to generate spatially graded structures of polymers. It has been shown that graded morphologies can be generated by introducing a spatial gradient of the quench depth into the phase separation process of polymer mixtures. In this particular case, the gradient of quench depth can be generated by using either a temperature gradient which sandwiches the phase boundary⁶ or by a gradient of light intensity⁷⁻⁹. Furthermore, by taking advantage of gravity, polymers containing a spatial gradient of nanogels were fabricated using the self-floating property of the gel¹⁰. It has been shown that photopolymerization combined with curing reactions can be also utilized to create a lateral gradient of pore size on the polymer surface¹¹ or a continuous gradient of modulus along the sample length¹². Experiments on spatially graded polymers in the bulk state of polymer blends¹³ as well as the polymer with gradient surfaces¹⁴ have been recently reviewed. The investigation on stationary morphology and the kinetics of phase separation in multi-component polymer systems becomes available in 3-D thanks to the developments of laser-scanning confocal microscopy (LSCM)¹⁵ combined with fluorescence spectroscopy¹⁶.

In the previous studies, we have utilized photodimerization of anthracene to cross-link one polymer component in the bulk state of binary polymer blends to kinetically control the phase separation process¹⁷. The resulting morphology was subsequently observed by phase-contrast optical microscopy and analyzed by the 2D fast Fourier Transform (2D-FFT). However, there are two drawbacks for the experimental methods described in previous experiments. The 3-D information on the spatially graded morphology was not available for the bulk state of polystyrene/poly(vinyl methyl ether) blends in the experiments using phase-contrast optical microscopy.⁷ Furthermore, only partially bi-continuous morphology was obtained for polystyrene/methyl methacrylate mixtures observed under LSCM.⁸ The morphology obtained in these experiments is composed of bi-continuous structure at the high end of the light intensity gradient, whereas dispersed-phase morphology emerges at the low end of this intensity gradient. From the viewpoint

of materials science, polymers with thoroughly 3-D bi-continuous morphologies are highly expected for designing specialty polymers.

In this paper, we demonstrate that by combining the Lambert-Beer law with photopolymerization-induced phase separation, polymer networks with *uni-axially* graded morphology exclusively along the Z-direction (the propagation direction of light) can be generated and controlled by changing the irradiation intensity. Furthermore, by utilizing the computer-assisted irradiation (CAI) techniques¹⁷, the *uni-axially* graded morphology exclusively in the XY plane was also constructed. The formation of these gradient structures was *in situ* monitored by laser-scanning confocal microscopy (LSCM) and their kinetic processes are analyzed and discussed by the method using the correlation function concept. Finally, we will discuss the possibility of architecturing polymers with *bi-axially* graded morphology by combining the CAI techniques and high irradiation intensity.

Experimental section

Materials and methods.

Polymers used in this study are Rhodamine B-labeled poly(ethyl acrylate) with anthracene (PEA-AR) and without anthracene (PEA-R) as a side group. The chemical structure of these polymers is shown in **Figure S1** of the Supporting Information. Here, anthracene was used as a photo-cross-linker, which undergoes dimerization upon irradiation with 365 nm UV light. This photochemical reaction serves as a stopper of polymer diffusion, resulting in the formation of PEA networks

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by which the transient morphology induced by photopolymerization can be efficiently frozen. Otherwise, the resulting gradient morphology is frozen by the increase in viscosity associated with the polymerization. The chemical synthesis and the labeling procedure were described in detail elsewhere¹⁸. In this study, PEA-R ($M_n = 1.6 \times 10^5$, $M_w/M_n = 2.3$) and PEA-AR ($M_n = 1.7 \times 10^5$, $M_w/M_n = 2.2$) were synthesized and used as a polymer component of the mixture. The average label content of anthracene (A) obtained for PEA-AR is 2.2 anthracene moieties per chain. The characteristics of these samples are given in **Table 1**. It should be noted that the network formation of the PEA-AR component can be tuned

Polymer	M_n	M_w/M_n	α	EGDMA
PEA-AR	1.7×10^{5}	2.2	2.2	$2 \mathrm{~wt\%}$
PEA-R	1.6×10^5	2.3	—	

Table 1. Characteristics of polymers used in this experiment.

- "A" and "R" stand respectively for anthracene and rhodamine B.

 α is the average number of anthracene moieties labeled per a PEA-AR chain.

by irradiation with 365 nm UV light. Therefore, the presence of anthracene on the poly (ethyl acrylate) component could enhance the freezing efficiency of the transient morphologies via the network formed by photodimerization of anthracene. Monomer methyl methacrylate (MMA) was purified by the conventional method as

described previously.¹⁹ The labeled polymers were dissolved in purified MMA monomer containing photoinitiator Lucirin TPO (BASF Inc., used without further purification). Subsequently, the solution was injected slowly into a home-made glass cell prior to the experiments. All the experiments were carried out at 25°C.

Visible light attenuator: In order to generate a strong gradient of light intensity inside the mixture using visible light, perylene (Wako Chemicals Inc, Tokyo, recrystallized using toluene) was added into the mixture as a light absorber. Attenuation of light with the wavelength 405 nm from the digital projector can be adjusted by controlling the amount of perylene in the mixture.

Computer-Assisted Irradiation (CAI) Method.

We have developed the so-called computer-assisted irradiation (CAI) apparatus to trigger and control the phase separation in both space¹⁷ and time¹⁹ using visible light from a digital projector. As shown in **Figure 1**, a light pattern with a predetermined geometry was first designed and generated on the computer **1**. Subsequently, this light pattern was sent from a projector having a digital light processing (DLP)-unit where movements of micro-mirrors arrays can be controlled by computer (Texan Projector, Model KG-PS233X, Kaga Electronics, Tokyo). This designed light pattern was projected through a set of lenses onto a mixture placed under a modified phase-contrast optical microscope (Nikon, Model Eclipse TE2000-U) as shown in Fig. 1. The time- evolution of the phase separation



Figure 1. Block diagram of the computer-assisted irradiation (CAI) apparatus.

process induced by this procedure was *in situ* recorded on the computer 2 where subsequent data processing and analysis were performed. By using this set up for polymerization-induced phase separation, the *uni-axially* graded structure exclusively in the X-Y plane illustrated in Figs. 2(a) can be generated and controlled by irradiation with low light intensity. This can be realized with the condition under which the effect of the light-intensity gradient along the Z-direction is practically neglected. In addition, using this CAI apparatus, the *bi-axially* graded morphology inside the X-Y plane as well as along the Z-direction can be simultaneously generated and controlled by using a strong light intensity. It is worth noting that using this CAI method, the geometry of the resulting morphology can be defined and determined by the geometry of the light patterns produced by the digital projector.

Irradiation experiments and observation by laser-scanning confocal microscopy (LSCM)

All the experiments were performed at 25 °C using a laser-scanning confocal microscope (LSM-5 Pascal, Zeiss Inc.). The 3D stationary bi-continuous structures obtained after irradiation over a long period of time (more than 60 min.) were observed under a LSCM using the excitation wavelength 543 nm from a He-Ne laser (Lasos-LGK, 1mW). The fluorescence intensity from the samples was detected in the range of wavelength longer than 505 nm using a high pass filter. For morphology with low magnification, $\times 40$ objective lens with NA= 0.75 (Carl Zeiss) was used, whereas an oil-immersion high magnification lens ($\times 63$ Plant Apochromat objective, NA= 1.4, Carl Zeiss) was for the observation at high The images with the size $(512 \times 512 \text{ pixel})$ were recorded with 8 magnification. bit gray scale (256 levels). The 3D images of the spatially graded morphology were constructed from the 2D images captured at different depths by using the software Imaris (Bitplane Scientific Solutions). Further detail of the measurements can be found in early publications^{8, 18, 20}

Observation of the gradient morphology by using LSCM.

In the time-resolved measurements, the mixture with the thickness ca. 70 μ m placed under the LSCM was excited from above using 365 nm UV light (300 W Hg-Xe lamp, Moritex Inc., Japan) through an optical fiber. The resulting morphology was scanned from below using the 543 nm line of a He-Ne laser equipped on the LSCM. For all the data shown in this manuscript, the origin of the Z-coordinate was taken as the position of the interface between the cover slip (non-fluorescent) and the sample The sudden increase in the fluorescence intensity upon passing the (fluorescent). glass *coverslip-sample interface*, was used to determine the origin of the Z-axis. All the distances indicated in the morphologies hereafter were measured from this origin. The 3D spatially graded morphology was monitored at three different positions equally separated by 21 µm along the direction of the incident UV light. The "upper" position is closer to the light source (under higher light intensity) and the "lower" position is farther (under lower light intensity) from the light source. Scanning was performed during irradiation from the "upper" to the "lower" positions and was repeated over again until the morphology became frozen. For each position, scanning was performed over four times and these data were averaged The time required to accomplish one scan is 3.9 s and to obtain the final results. the time-lag between scanning is 1.0 s. Irradiation took about 60 min for high intensity and 90 min for low intensity to achieve the stationary morphology. The geometry for irradiation and observation is illustrated in **Figures 2**. The data were



Figures 2

Figure 2. Schematic representation of the co-ordinates used for irradiation and morphological observation by laser-scanning confocal microscopy (LSCM). The red arrows indicates the direction of the morphological gradient. The direction of the gradient is controlled by the direction of the light intensity in the patterns.

then collected on a computer (Dell Computer, Model Vostro 1200) prior to the analysis of phase separation kinetics. Further experimental details were provided in previous publications.

Results and Discussion

Polymerization kinetics of MMA in the mixtures

The overall polymerization yield $\Phi(t_{irr})$ of the mixture was *in situ* monitored by following the disappearance of the C=C bonds of MMA monomer using FT-IR spectroscopy upon irradiation²¹. The yield $\Phi(t_{irr})$ was calculated from the following equation:

$$\Phi(t_{irr}) = \begin{pmatrix} \frac{(A_{C=C})_{t_{irr}}}{(A_{C=O})_{t_{irr}}} \\ 1 - \frac{(A_{C=C})_{t=0}}{(A_{C=O})_{t=0}} \end{pmatrix} \times 10^2$$
(3)

where A expresses the absorbance of the C=C double bonds of MMA monitored at 1640 cm⁻¹. In order to compensate for a small difference in thickness among samples, all the absorption data were normalized using the absorbance of the C=O bond which does not involve in the polymerization. The experimental results obtained under various irradiation intensities ranging from 0.01 to 0.1 mW/cm² are shown in **Figure 3(a)** where the derivative $(d\Phi/dt)$ of the polymer yield with respect

Figures 3(a) & 3(b)

to irradiation time was also illustrated in the same figure. From these experimental



Figures 3. (a): Polymerization kinetics of MMA and its mean rate observed for a PEA-AR/MMA (9/91) mixture obtained by irradiation using 365 nm UV light with the intensity ranging from 0.01 to 0.1 mW/cm² at 25 °C; (b): Dependence of the characteristic time τ of the Trommsdorff-Norrish effect on the irradiation intensity.

results, it was found that the polymerization yield of PMMA in a PEA-AR/MMA (9/91) mixture exhibits a typical auto-acceleration behavior, the so-called Trommsdorff- Norrish effect²²⁻²³ during irradiation. The yield Φ first increases with irradiation time, and then quickly uprised at a particular irradiation time τ , revealing the autocatalytic behavior of the photopolymerization. Eventually, Φ reaches a stationary state at long irradiation time.

From Fig. 3-a, it was found that the characteristic time τ at which the auto-acceleration process occurs, becomes shortened as the light intensity increases. The dependence of τ on the irradiation intensity is illustrated in Figure 3(b), showing that the Trommsdorff-Norrish effect appears earlier as the irradiation intensity becomes higher. This behavior is the essential feature of the conventional free radical polymerization and arises from the interplay between the increase in viscosity associated with the reaction and the termination step of polymerization. As described later, since the morphology of the mixture evolving with irradiation time is frozen after this characteristic time τ , the above kinetic data suggest that polymerization could be utilized as a useful tool for the morphology control by varying the light intensity.

Results and discussion

Dependence of the stationary graded morphologies on the light intensity.

As reported previously^{24, 25}, polymerization-induced phase separation is a competing phenomenon between the two antagonistic processes: polymerization and phase

separation. The resulting morphology is therefore determined by this competition. If the polymerization overcomes the phase separation process, the resulting morphology will be frozen by the increase in viscosity of the polymerizing mixture, providing a useful tool for morphology control. In contrary, if the phase



separation process surpasses the polymerization (e.g. for polymers having T_g lower than the experimental temperature), the final morphology would be two-phase

random structures. Therefore, the stationary morphology obtained along the propagation direction of light would reveal the fingerprint of the phase separation induced by polymerization under the gradient of light intensity. **Figure 4(a)** shows

Figure 4. (a) Dependence of the stationary (final) graded morphology on the irradiation intensity ranging from 0.01 ~ 0.15 mW/cm² observed at three different depths (Z) along the thickness direction of a PEA-AR/MMA (9/91) mixture. (b): Dependence of the stationary length scale ξ_{∞} on the irradiation intensity observed at various depths of the sample during irradiation.

the stationary (final) gradient morphology observed for a PEA-AR/MMA (9/91) mixture undergoing phase separation induced by irradiation using 365 nm UV light with various intensities ranging from $I = 0.01 \sim 0.15 \text{ mW/cm}^2$. The Z-coordinate in the figure indicates the depth of observation in the sample with the front (upper) surface/cover glass interface taken as the origin. From the results illustrated in Fig. 4(a), it was found that similar stationary morphology *repeatedly* emerges at different Z-coordinates along the diagonal direction of the morphology map. Namely, the morphology, the co-continuous structure for example, which appears in the shallower region (close to the light source) under low irradiation intensity emerges again in the deeper region (far from the light source) under high irradiation intensity. It is worth noting that similar evolution of the morphology of polymer blends on the viscosity-composition diagram was proposed to predict the experimental conditions for the emergence of bi-continuous morphology during processing²⁶. For the same depth Z=30.4 µm, the characteristic morphologies emerge in the following order: wetting layer $(I = 0.01 \text{ mW/cm}^2) \rightarrow salami \text{ structure } (I = 0.03 \text{ mW/cm}^2) \rightarrow$ bi-continuous structure ($I = 0.15 \text{ mW/cm}^2$) as the light intensity increases. These morphologies eventually reached a stationary state after a certain irradiation time. It was also found that similar structures were reproduced in the same fashion at other depths Z=21.6 and 12.8 μ m (at lower intensity and shallower positions). This variation of morphology with the light intensity resembles the case of irradiation with uniform intensity 27 . Because similar morphology repeatedly emerges at different light intensity, irradiation time and depth in the same sample, the experimental results illustrated in Figs. 4 would serve as a guide for morphology control using polymerization-induced phase separation. The dependence of these stationary length scales on irradiation intensity is summarized in **Figure 4(b)**, where the gradient of the resulting morphology is almost constant and the same, except the case of the highest intensity ($I = 0.15 \text{ mW/cm}^2$). Under high light intensity, the resulting molecular weight of PMMA is relatively small and as a consequence, its high mobility might generate some sort of local flux which could disturb the gradient set up by the light intensity. It is worth noting that the utilization of polymers with spatially graded structures has been proposed for the useful combinatorial methods in materials synthesis as well as pharmacological

studies²⁸⁻³¹. On the other hand, as reported previously, when the characteristic length of the morphology increases and approaches the sample thickness, wetting phenomena could interfere with the phase separation process^{20, 27.} This leads to the formation of very large phase domains, i.e. the so-called wetting layer ³² at late stage of phase separation as described in the next section.

Formation kinetics of the morphology spatially graded along the Z-direction. As described in the Experimental Section, the formation process of the graded morphology at three different positions equally separated by 21 μ m from the origin of the Z-axis was *in situ* observed along the irradiation (Z) direction. These particular positions are respectively indicated as "*upper*", "*middle*" and "*lower*" with respect to the direction of the incident light. Namely, among the three positions,

Figure 5. (a): Irradiation-time evolution of the graded bi-continuous morphology of a PEA-AR/MMA(7/93) mixture observed by LSCM at three different positions along the Z-direction equally separated by 21 μ m under irradiation with 405 nm visible light. The number on the top of the figure indicates the net irradiation time.

the light intensity is highest at the position "*upper*" and is lowest at the position "*lower*". As shown in **Figure 5(a)**, it was found that upon irradiation with 365 nm, UV light with the intensity 0.10 mW/cm², the resulting morphologies of a PEA-AR/MMA (7/93) mixture are bi-continuous with the characteristic length ξ increasing with irradiation time and eventually reached a stationary state as shown in

Figure 5(b). In order to understand the formation kinetics of these spatially graded structures, the net time of the phase separation process was defined as $(t-t_0)$ where t is irradiation time and t_0 is the irradiation time corresponding to the onset of the phase separation process. It is worth noting that the method of determining t_0 was based on the sudden change in the fluorescence intensity upon passing the phase boundary of the mixture²¹. It was found that at the early stage of the photopolymerization process, i.e. for short irradiation time, the characteristic length scale ξ does not significantly change with the irradiation time t_{irr} .

Figure 5. (b): Formation kinetics of the spatially graded bi-continuous morphology obtained in Fig. 5(a) monitored at different depths in the mixture. ξ is the characteristic length scale of the bi-continuous morphology.

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Subsequently, ξ quickly increases with t_{irr} and eventually reaches a stationary state. The kinetics of the phase separation process can be approximately expressed by the power law $\xi \sim (t-t_0)^a$ where *a* is the exponent expressing the steepness of the gradient formed in the bi-continuous structures. Careful look at the data reveals the deviation from the power law of the phase separation kinetics. For comparison, the slope *a* =1 and 1/3 are drawn as a straight line in the figure. The former was proposed by Siggia taking into account of surface tension³³, whereas the latter is known as Slyosov-Lifshitz-Wagner mechanism for the Oswaldt ripening

process^{34, 35}. The deviation from the power law is significant in the "*upper*" region close to the light source. The critical dynamics of a non-conserved system undergoing polymerization followed by continuous volume shrinkage³⁶ would be responsible for this particular behavior. As far as observed under the laser-scanning confocal microscope, the above results indicate that polymers with bi-continuous morphology having gradient characteristic length scales ranging from few micrometers to hundreds of micrometers can be generated and controlled by using photopolymerization.

Uni-axially graded morphology generated exclusively in the X-Y plane by the CAI method.

A mixture containing 2 wt% of Lucirin TPO was irradiated using 405 nm visible light with the intensity distribution illustrated in **Figure 6(a)**. The stripe pattern

Figure 6. (a): Intensity distribution of the light pattern used to generate uni-directional graded morphology along the X-axis; (b): The uni-axially graded morphology exclusively along the X-direction in response to the light pattern shown in (a); (c): The spatial variation of the characteristic length scales obtained by analysis using the CF method; (d): 3D morphology of the bi-continuous morphology exclusively graded along the X-direction as expressed by the arrow.

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of visible light intensity with a gradient along the X-axis and with a constant intensity along the Y-axis was impinged onto the mixture placed under a microscope by using the digital projector illustrated in Fig.1. The light intensity gradient was programmed so that at $I=3.0 \text{ mW/cm}^2$ and 0.5 mW/cm² at two ends of the intensity gradient, and the light stripe at the center has a linear gradation of 1.3×10^{-2} mW/ μ m⁻¹ over a width of 190 μ m as shown in Fig. 6(a). The stationary morphology obtained by irradiation over 60 min is shown in Fig. 6(b), revealing the uni-directionally graded bi-continuous morphology obtained for a PEA-R/MMA (11/89) mixture in response to the light pattern shown in Fig. 6 (a). As expected, the bi-continuous structures with a gradient of characteristic length scales exclusively along the X-axis emerge, whereas the periods of the continuous structures along the Y-axis remain the same for a given X-coordinate. Furthermore, from the observation along the X-Z and Y-Z planes, it was found that the bi-continuous morphologies are spatially uniform in these two planes. It should be noted that in principle, by inducing phase separation using light stripe patterns constructed by the CAI method shown in Fig. 6(a), the anisotropic (directional) spinodal structures can be generated in a given (XY) plane of the sample. Particularly, the direction of these bi-continuous structures can be controlled by varying the orientation of the light stripe patterns as revealed in Fig.6(b), suggesting a novel way to design polymers with anisotropic transport properties taking advantages of the continuity of morphology.

By the analysis using the correlation function (CF) method described above, the

characteristic length scales of the directional bi-continuous structures along the X-axis were obtained and illustrated in Figure 6(c). From this analysis, it was found that the periods of the unidirectional bi-continuous morphology are almost unchanged in the first 100 µm of the irradiated portion of the sample. This period gradually increases upon moving from the regions of higher light intensity to the regions of lower light intensity in correspondence to the intensity profile shown in These results suggest that the polymerization-induced phase separation Fig. 6(a). can be used to design polymer films with controllable mechanical properties such as flexural modulus as well as optical properties such as transparency and reflection. The 3D image of a PEA-R/MMA (11/89) mixture obtained by photo-polymerization was constructed by using the software Imaris^R and is shown in **Figure 6(d)**. Obviously, the uni-directionally bi-continuous structure of the mixture was exclusively generated along the X-direction in the (XY) plane of the mixture as indicated by the arrow drawn in the figure.

Co-continuous morphology uni-axially graded along the Z-direction constructed by the CAI method: the use of visible light absorber.

In order to promote the formation of graded morphology along the Z-axis for a PEA-R/MMA (11/89) blend using the CAI method, perylene, a relatively stable visible light absorber, was added into the mixture to generate and control the gradient of the incident light intensity inside the mixture. Shown in **Figure 7** (a) are the morphologies of a PEA-R/MMA (11/89) mixture with a gradient of

bi-continuous structures generated along the Z-direction by irradiation with two different intensities I = 3.0 and 9.0 mW/cm² at 405 nm. The spatially graded morphologies were clearly revealed along the thickness (Z) direction of the mixtures. It should be noted that these structures are stationary and were obtained by irradiating the mixtures with 405 nm over 60 min. Since the morphology is uniform within the X-Y plane for a given depth (Z-coordinate), the 2D-FFT was used to analyze these structures. The 2D-FFT power spectra of these morphologies are shown in the insets of Figs. 8(a). The significant effects of light intensity gradient on the characteristic length scales of the bi-continuous morphologies are depicted in **Figure 7(b)** for four different intensities ranging from 3.0 to 9.0 mW/cm².

Figure 7. (a): Uni-axially graded co-continuous morphology along the Z-axis obtained for a PEA-R/MMA(11/89) mixture containing 0.08 wt% of perylene observed under irradiation with 405 nm from the digital projector with two intensities 3.0 and 9.0 mW/cm²; (b): Gradient of the characteristic length scales of the stationary bi-continuous morphology obtained for a PEA-R/MMA(11/89) mixture under irradiation with different light intensities ranging from $3.0 \sim 9.0 \text{ mW/cm}^2$.

Except in the region close to the sample surface from the side of the incident light, the phase separation promotes quicker in deeper locations. For the same depth, the length scales become larger for locations receiving lower light intensity. These experimental results suggest an experimental strategy to design graded polymer materials with novel functionalities using photopolymerization.

Since the absorption of the mixture at 405 nm is weak and not enough to build into the mixture a wide range of intensity gradients for the design of graded bi-continuous morphologies, a small amount of perylene, a chromophore which can serve as an absorber of visible light, was added into the mixtures to enhance the light intensity gradients inside the sample. The useful roles of perylene as a light absorber in constructing graded morphologies are revealed in Figure 8(a) where the mixture containing 0.08 wt% of perylene clearly exhibits a gradient of bi-continuous structures at three positions 6, 40 and 68 µm along the Z-direction, whereas the mixture without perylene shows only spatially uniform bi-continuous morphology at the same locations. As indicated in **Figure 8(b)**, variation of the characteristic length scales ξ of these bi-continuous morphologies obtained along the Z-direction by using 2D-FFT justifies the advantage of using perylene as a light absorber. The 3D structure corresponding to the morphology shown in Fig. 8(a) containing 0.08 wt % of perylene is illustrated in **Figure 8(c)**. To facilitate the vision, the 3D stationary bi-continuous structure was partially cut and "peeled off" at different depths (Z-coordinates) to reveal the inner structures. It was found that the morphology obtained by this way exhibits the bi-continuous structures with short periods on the top (closer to the light source), which continuously extend to the bottom (farther from the light source) of the mixture while the period of the structures becomes larger towards the bottom (Z-direction).

Figure 8. (a) Effects of doping perylene on the gradient bi-continuous morphology of a PEAR/MMA(11/89) mixture. Right: without perylene; Left: with 0.08 wt % of perylene; (b) Evidence for the effect of perylene added into the mixture on the characteristic length scale; (c): 3D uni-directionally graded morphology of the above mixture containing perylene irradiated with the light intensity 3.0 mW/cm². The arrow indicates direction of the graded structure.

The unidirectional gradient structure exclusively in the XY plan shown in Fig.6 (d) and unidirectional gradient morphology exclusive along the Z-direction illustrated in Fig.8 (a) suggest that bi-axially gradient morphology can be constructed and controlled by the combination of these two irradiation techniques. By inducing phase separation process in polymer using the combination of these two irradiation of these two irradiation methods, polymer materials with interesting transport properties could be obtained. Actually, we have obtained these polymers and IPNs with such a bi-axially and bi-continuous morphology. Since the morphology analysis is currently unavailable, these results will be published in a near future.

Conclusions

Polymers with bi-continuous gradient morphology were designed and controlled by photo-polymerization of methyl methacrylate monomer containing a poly(ethyl acrylate) derivative. The following results were obtained.

(1) By taking advantages of the gradient of quench depth resulting inside the mixture via the Lambert-Beer law, *uni-axially* graded bi-continuous morphology exclusively along the thickness direction (Z) of the sample can be simply generated by irradiation with strong light intensity. Similarly, graded bi-continuous structures can be also generated exclusively in the (XY) plane by using the computer-assisted irradiation (CAI) techniques with moderate light intensity. In particular, an

analysis method using spatial correlation function was developed to analyze these spatially graded structures.

2) By combining the CAI techniques with the addition of perylene into the polymerizing mixture, *bi-axially* graded co-continuous morphology can be generated and controlled. Thus, the combination of light absorber with the CAI techniques opens a possibility of designing polymer mixtures with *multi*-axially gradient structures.

3) The time-resolved data obtained by laser-scanning confocal microscopy show that the phase separation starts from the region with low light intensity (*bottom*) first and then gradually expanded to the regions with high light intensity (*front*), suggesting the contribution of some local osmotic pressure induced by the gradient of polymer yield in the mixtures.

Supporting Information

Additional details of the polymer structure, the morphology analysis and the detailed analysis method using the correlation function approach are separately provided.

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References

- (1) M. Shen and M.B. Bever, J. Mater. Sci., 1972, 7, 741-746.
- (2) G. Akovali, K. Biliyar and M. Shen, J. Appl. Polym. Sci. 1999, 73, 1721-1725.
- (3) Y. Agari, M. Shimada, A. Ueda, Macromol. Chem. Phys. 1996, 197, 2017-2033.
- (4) Interpenetrating Polymer Networks, ed. D. Klempner, L.H. Sperling and L.A. Utracki, Adv. Chem. Ser. No. 239, Amer. Chem. Soc., Washington DC. 1994.
- (5) Y.S. Lipatov and T. Alekseeva, *Phase-Separated Interpenetrating Polymer Networks: Adv. Polym. Sci.* **208**, Springer, Berlin 2010.
- (6) J. Okinaka and Q. Tran-Cong, *Physica D*, 1995, 84, 23-30.
- (7) H. Nishioka, K. Kida, O. Yano and Q. Tran-Cong, *Macromolecules* 2000, 33, 4301--4303.
- (8) H. Nakanishi, N. Namikawa, T. Norisuye and Q. Tran-Cong-Miyata, *Soft Matter* 2006, 2, 149-156.
- (9) G. Noblet, N. Désilles, L. Lecamp, P. Lebaudy, C. Bunel, Macromol. Chem. Phys. 2006, 207, 426-433.

- (10) C. Chen, J. Liu, F. Sun, J.W. Stansbury, J. Polym. Sci. Part A: Polym. Chem.
 2014, 52, 2830-2840.
- (11) K. Kreppenhofer, J. Li, R. Segura, L. Popp, M. Rossi, P. Tzvetkova, B. Luy, C.J. Kähler, A.E. Guber; P.A. Levkin, *Langmuir* 2013, *29*, 3797-3804.
- (12) K.U. Claussen, R. Giesa, H.-W Schmidt, *Polymer* 2014, 55, 29-38.
- (13) J. Genzer and R.R. Bhat, in *Soft Matter Gradient Surfaces: Methods and Applications*; ed. J. Genzer, John Wiley& Sons Inc., New Jersey, 2012, Chapter 2, pp. 19-46.
- (14) D. Fujiki, C. Jing, D.-T. Van-Pham, H. Nakanishi, T. Norisuye, and Q.
 Tran-Cong-Miyata, *Adv. Nat. Sci.: Nanosci. Nanotechnol.* 2010, 1, 043003 (7 pp).
- (15) Handbook of Biological Confocal Microscopy; ed. James Pawley, 3rd Edition, Springer, New York, 2006.
- (16) Joseph R. Lakowicz, Principles of Fluorescence Spectroscopy; 2nd Edition;
 Plenum, New York, 1999.
- (17) S. Ishino, H. Nakanishi, T. Norisuye and Q. Tran-Cong-Miyata, Macromol. Rapid Commun. 2006, 27, 758-762.
- (18) H. Nakanishi, M. Sato, T. Norisuye and Q. Tran-Cong-Miyata, *Macromolecules* 2004,
 37, 8495 8498
- (19) Q. Tran-Cong-Miyata, D.-T. Van-Pham, K. Noma, T. Norisuye and H. Nakanishi, *Chinese J. Polym. Sci.* 2009, **26**, 23-36.
- (20) T. Shukutani, T. Myojo, H. Nakanishi, T. Norisuye and Q. Tran-Cong-Miyata, *Macromolecules* 2014, **47**, 4380-4386.

- (21) H. Nakanishi, M. Sato, T. Norisuye and Q. Tran-Cong-Miyata *Macromolecules* 2006, **39**, 9456 9466.
- (22) J.P. Flory, *Principles of Polymer Chemistry*, Cornell University Press, Ithaca, New York, 1953, Chapter IV, pp. 124-129.
- (23) R.J. Young and P.A. Lovell, *Introduction to Polymers*, CRC Press, Boca Raton, Florida,2011, Chapter 4, pp. 71-77.
- (24) Q. Tran-Cong and A. Harada Phys. Rev. Lett. 1996, 76, 1162-1165.
- (25) A. Harada and Q. Tran-Cong, *Macromolecules* 1997, **30**, 1643-1650.
- (26) R.W. Renfree, T.J. Nosker, D.R Morrow, K.E. Van Ness and L.W. Suttner, *SPE ANTEC* 1992; pp. 2396-2400.
- (27) N. Kimura, K. Kawazoe, H. Nakanishi, T. Norisuye and Q. Tran-Cong-Miyata,
- Soft Matter 2013, 9, 8428-8437.
- (28) J.C. Meredith, A. Karim and E.J. Amis, *Macromolecules* 2000, **33**, 5760-5762.
- (29) Takeuchi, I.; Lauterbach, J.; Fasolka, M.J. Mater. Today 2005, 8, 18-26.
- (30) J.C. Zhao Progr. Mater. Sci. 2006, **51**, 557-631.
- (31) J.C. Meredith, A. Karim and E.J. Amis, *Macromolecules* 2000, 33, 9747-9756.
- (32) F. Chen, Y. Zhang, W. Shi, Y. Liang and C.C. Han, *Polymer* 2010, **51**, 6030-6036.
- (33) E.D. Siggia, Phys. Rev. 1979, 20, 595-605.
- (34) I.M. Lifshitz and V.V. Slyosov, J. Phys. Chem. Solids 1961, 19, 35-50.
- (35) C.Z. Wagner, Z. Elektrochem 1961, 65, 581-594.
- (36) K. Kinohira, D.-T. Van-Pham, A. Hirose, T. Norisuye and Q. Tran-Cong-Miyata,

Curr. Opin. Solid State Mater. Sci. 2011, **15**, 254-261.

Graphical Abstract

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3D uni-axially graded bi-continuous morphology obtained for a Rhodamine B-labeled poly(ethyl acrylate)/methyl methacrylate (PEAR/ MMA (11/89) mixture along the Z-direction generated by the computer-assisted irradiation (CAI) method.

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Polymer Blends with Uni-axially and Bi-axially Graded Bi-continuous

Morphology Designed by Photopolymerization-Driven Phase

Separation

Atsuko HIROSE, Keisuke SHIMADA, Chie HAYASHI, Hideyuki NAKANISHI, Tomohisa NORISUYE, Qui TRAN-CONG-MIYATA^{*}

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