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Interpenetrating Polymer Networks with Spatially Graded Morphology Controllable by UV-Radiation Curing

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Summary: Interpenetrating Polymer Networks (IPNs) composed of polystyrene (PS) and poly(methyl methacrylate) (PMMA) were synthesized from a precursor mixture by using dissimilar photo-cross-link reactions. When the reation yields exceeded a certain threshold, the mixture was quenched from one-phase region into two-phase region, leading to phase separation. Upon irradiation with strong UV-light, an intensity gradient was formed along the propagating direction of the exciting light, generating a gradient of quench depth via the spatial inhomogeneity of the cross-link reactions. As a consequence, a gradient of the characteristic length scales was continuously generated from the top to the bottom of the mixture. The resulting three-dimensional (3-D) morphology was *in-situ* observed at different depths of the mixture by using a laser-scanning confocal microscope (LSCM). From this 3-D observation, it was found that phase separation was accelerated at the bottom of the mixture and proceeded in an autocatalytic fashion. The mechanism for the formation of the graded morphology was discussed in conjunction with the kinetics of the autocatalytic phase separation.

Keywords: autocatalytic phase separation; autocatalytic reaction; graded bi-continuous morphology; interpenetrating polymer networks; photo-cross-linking; photopolymerization

Introduction

Materials with spatially graded structures have been a subject of the research field called *functional graded materials*.[1] It has been demonstrated that these materials exhibit properties such as heat insulation or high impact strength superior to those with uniform structures. Significant properties revealing by spatially graded structures can be found in nature such as the mechanical properties of wood, nacre etc.[2] The mechanism for the emergence of these spatially graded structures takes root from the inhomogeneous kinetics of their formation process occuring over very long time scale and very large length scale. In order to design and control the spatial distribution of morphology in multiphase polymers, we have coupled spatially non-uniform reactions to the phase separation process of polymer mixtures. Photochemical reactions provide an efficient tool for this particular purpose. In this study, by taking advantages of a gradient of light intensity, a variable gradient of quench depths was introduced into a phoreactive mixture to control its phase separation kinetics. The resulting spatially graded morphology and the phase separation kinetics induced by this gradient of light were monitored three-dimensionally using a laser-scanning confocal microscope (LSCM) with contrast-enhancement by selectively labeling one polymer compo-

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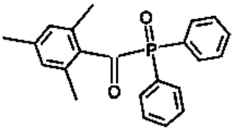
nent with a fluorescent dye. Morphology and phase separation kinetics under thermodynamically non-uniform conditions are discussed together with the effects of the reaction autocatalysis on the phase separation process.

Experimental Setup

Poly(*cross*-styrene)-*inter*-/poly(*cross*-methyl methacrylate) IPNs were synthesized from a homogeneous solution containing methyl methacrylate (MMA) and photoreactive polystyrene by using two independent photo-cross-link reactions. The PMMA networks were generated by photopolymerization of MMA using Lucirin TPO (BASF) **1** as a photoinitiator and ethyleneglycol dimethacrylate (EGDMA) as a cross-linker. The concentrations of Lucirin and EGDMA were kept at 2 wt % with respect to the total weight of MMA monomer. Polystyrene bearing both anthracene as a photo-cross-linker and fluorescein as a marker for contrast enhancement (PSAF, $M_w = 1.05 \times 10^5$, $M_w/M_n = 2.1$) **2** was synthesized according to the procedure reported previously.[3]



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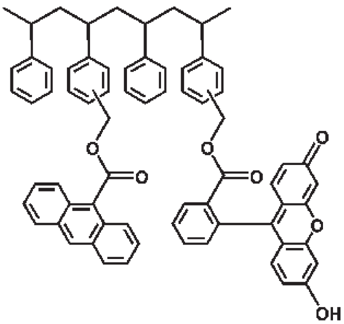

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PSAF was dissolved in MMA containing a given composition of PSAF and concentrations of Lucirin TPO and EGDMA. This homogeneous mixture was sandwiched between two coverslips and its thickness was kept at ca. 18 μm by an aluminum spacer. The sample was mounted into the heating block thermostated at 30°C on the stage of a laser scanning confocal microscope (inverted type, LSM 5 PASCAL, Carl Zeiss). Subsequently, the mixture was irradiated with 365 nm UV-light from a high pressure mercury lamp (350W, Moritex, Japan) through an optical fiber. This set-up allows the *in situ* observation of the morphology under irradiation. Upon UV irradiation, anthracene moieties attached on PSAF photodimerize, resulting in photo-cross-linked PSAF networks. Simultaneously, photo-polymerization and photo-cross-link reaction of MMA monomer were initiated by Lucirin TPO in the presence of the crosslinker EGDMA. As a consequence, when the reaction yields exceeded a critical threshold, the mixture was quenched from one-phase into two-phase regions, leading to phase separation. The resulting morphology was simultaneously scanned with 488 nm visible light from an Ar^+ ion laser. Fluorescein attached on the PSAF component was excited and fluoresces, providing a strong contrast for the PSAF-rich phase in the mixture. The morphology of the mixture was taken with the dimension (512 × 512 pixels) under 8-bit gray scale (256 levels). The resulting 2-D images were reconstructed into 3-D morphology by using the software Image Visart (v. 2.08, Carl Zeiss). The magnifications of objectives used in this study were ×40 (N.A. = 0.75, Carl Zeiss) and ×63 (Oil-immersion, N.A. = 1.40, Carl Zeiss) respectively for *in-situ* observation and 3-D image reconstruction. Analysis of the morphology was carried out by 2-D fast Fourier transform (2D-FFT) operating on the software Igor Pro (Wavemetrics Inc.) with a home-made macro-program. The resulting

2-D power spectra were circularly averaged to obtain the corresponding 1-D Fourier intensity distribution $I(q)$. The average characteristic length scale ξ of the morphology was calculated by using the Bragg condition $\xi = 2\pi/q_{max}$ where q_{max} is the wavenumber corresponding to the maximum Fourier intensity of the 1-D power spectra $I(q)$. In order to analyze the spatial gradient as well as the time-evolution of the morphology under irradiation, the 2-D images taken at different time and depths in the reacted mixtures were monitored and subsequently converted into 1-D power spectra. Further information on morphological observation and analysis was described in detail elsewhere.[4]

Result and Discussion

Spatially Graded Morphology Generated by a Gradient of Light Intensity

Upon irradiation using 365 nm UV light with weak intensity, e.g. 0.01 mW/cm^2 over 60 min, a PSAF/MMA(10/90) mixture underwent phase separation, exhibiting a bi-continuous morphology homogeneously dispersed throughout the reacting mixture. An example is shown in Figure 1 for the morphology taken at 4 μm apart from the top and the bottom of the irradiated sample. The origin of the Z axis located on the side of the incident UV light was determined from the change in the fluorescence intensity while scanning along the depth direction.[4] The bright regions in the micrographs represent the PSAF-rich phase which is identified using the fluorescence from the PSAF component, whereas the black domains correspond to non-fluorescent PMMA-rich phase. From careful examination of the 3-D morphology, it was found that the PMMA-rich-phase (black circles) are mutually interconnected, revealing the bi-continuous aspect of the morphology in the irradiated mixture.

As the irradiation intensity becomes higher, the mixture starts showing a gradient structure along the propagation direction (the Z-direction) of light. An example is shown in Figure 2 for a PSAF/MMA (10/90) mixture cross-linked with the intensity 0.06 mW/cm^2 at 30°C. As the focal plane was moved deeper into the mixture from the surface, the interdistance between the domains gradually increased, manifesting the spatial gradient of the morphology in the irradiated sample. In order to quantitatively evaluate the gradient morphology, the 2-D Fourier power spectra of these morphologies were converted into 1-D data as depicted in Figure 3. The peak position of the Fourier intensity shifts toward the side of smaller wavenumber along the Z-direction of the mixture, indicating that phase separation proceeded further upon approaching the bottom of the mixture. The distribution of the average characteristic length scales in the graded morphology obtained along the Z-direction is illustrated in Figure 4. Obviously, for all the light intensity, the characteristic length scales of the morphology in the mixture increase with the depth of the sample and become almost unchanged with the Z-direction in the vicinity of the bottom surface.

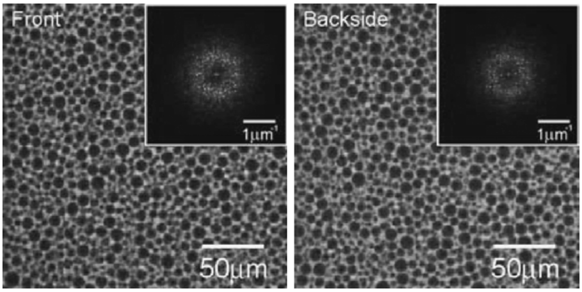

Figure 1.
Spatially uniform morphology obtained by irradiating a PSAF/MMA(10/90) mixture with weak intensity(0.01mW/cm^2). Indicated in the inset of each figure are the 2D-FFT power spectra of the corresponding morphology.

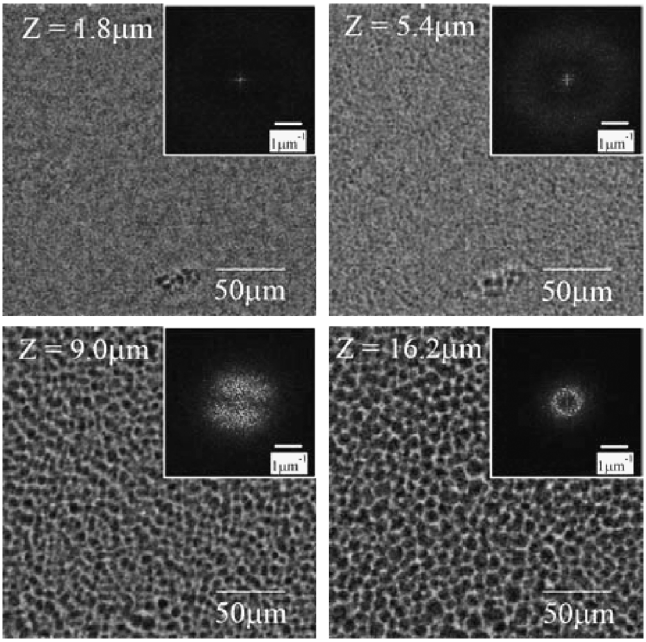

Figure 2.
Spatially graded morphology induced by irradiating a PSAF/MMA(10/90) mixture with strong intensity(0.06mW/cm^2). The domains coarsened along the propagation direction of the UV-light.

These experimental results suggest that the mixture was deeply quenched on the top portion of the sample and also the mobility in this portion rapidly decreases by the high intensity, whereas the mobility is less restricted due to the low yield of the reaction at the bottom portion of the mixture. Therefore, a gradient of quench depth

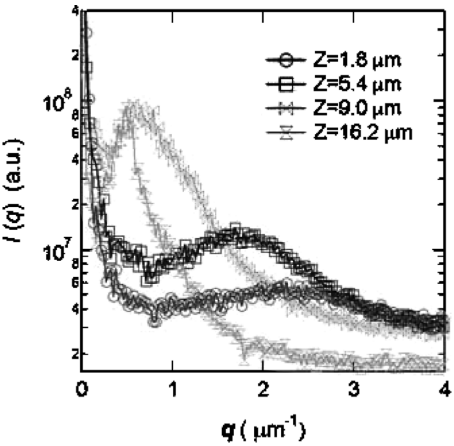

Figure 3.
Fourier intensity distribution of the graded morphology generated from a PSAF/MMA(10/90) mixture irradiated with 0.06mW/cm^2 UV-light.

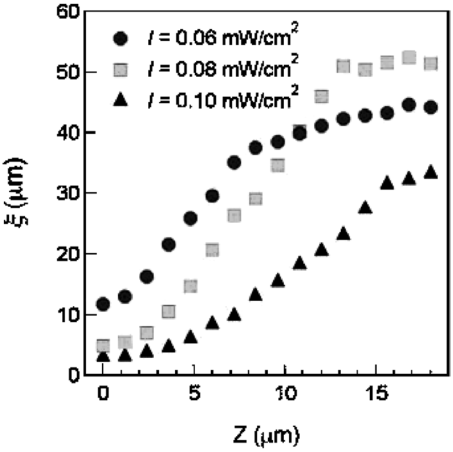

Figure 4.
The dependence of the spatial gradient of the average characteristic length scales on the irradiation intensity observed for a PSAF/MMA(5/95) mixture.

was formed along the Z-direction upon irradiation and as a consequence, morphology with a gradient of characteristic length scales was generated in the mixture as a strong light intensity was used for irradiation.

Three-dimensional visualization of the morphology with a spatial gradient of characteristic length scales can be constructed by stacking the morphology monitored at different depths in the reacting mixtures. An example is shown in Figure 5 for a 3-D image obtained for a PSAF/MMA (5/95) mixture irradiated with 0.1 mW/cm^2 UV light. Clearly, in the front (the side of incident light) of the sample, the characteristic length scales of the morphology are small and gradually increases along the depth direction. The dark interconnecting domains of the morphology in the left figure are the PSAF-rich phase, whereas the transparent domains represent the PMMA-rich phase. These PMMA-rich phases are also mutually interconnected through narrow channels stemmed from their interfaces.[3] These narrow channels were formed when the domains of PMMA-rich phase mutually approach at the late stage of phase separation and fails to merge with each other as the fraction of the PMMA networks exceeds a critical threshold.

Kinetics of Phase Separation Induced by a Gradient of Light Intensity

Phase separation induced by a gradient of UV light intensity was *in-situ* monitored under a LSCM at three different depths along the propagating direction of the UV-light. The 2-D morphology was monitored respectively at 2, 8, and 14 μm along the Z-direction of the mixture. Hereafter, these three positions for observation are respectively named "*top*", "*middle*", and "*bottom*" for convenience. The morphology induced by irradiation was repeatedly scanned from the "*top*" to the "*bottom*" position of the irradiated mixture until phase separation reaches a stationary state due to the cross-link reaction. Each micrograph was scanned for 3.9 sec accompanied by an interval of 3.3 sec which is required for changing the scanning at two different locations in the sample. In order to precisely investigate the kinetics of phase separation, the onset time of phase separation t_0 was obtained by measuring the "fluorescence cloud point" of the mixture under irradiation.[4] From these data, the phase-separation time $(t - t_o)$ was calculated where t is the irradiation time. For a PSAF/MMA (10/90) mixture, it was found that $t_0 = 398$ sec for the intensity 0.03 mW/cm^2. Figures 6 show the dependence of the

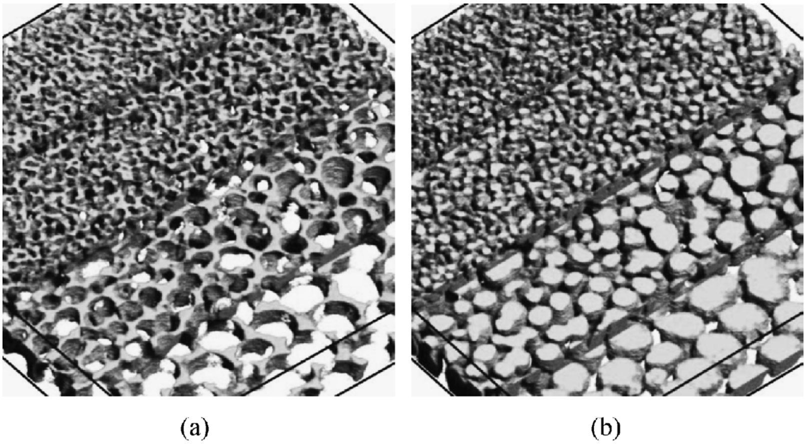
(a) (b)

Figure 5.
The 3-D graded morphology generated by irradiating a PSAF/MMA(5/95) mixture with 0.01mW/cm^2 light: (b) is obtained by contrast inversion of (a). Both phases are co-continuous.

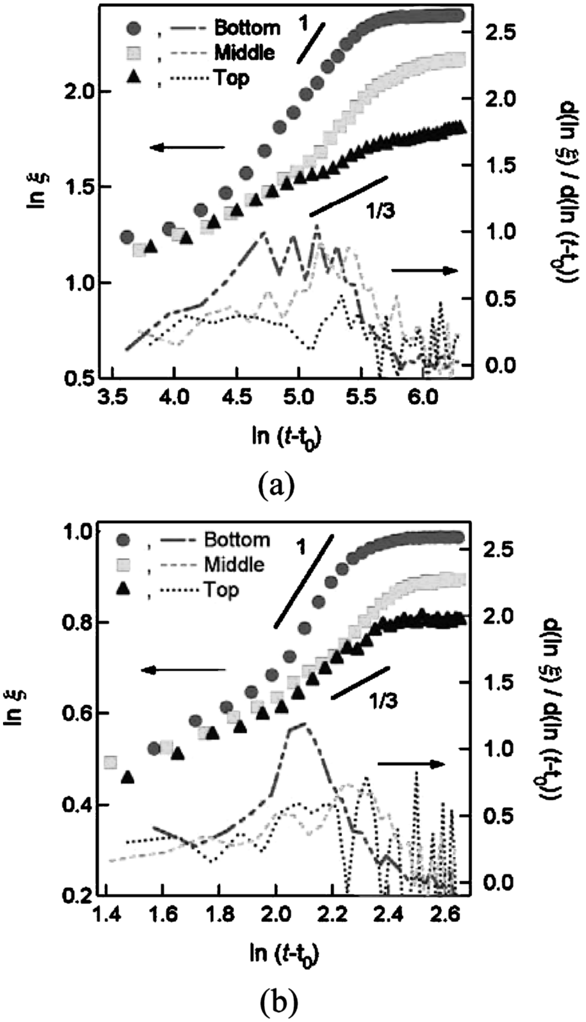

Figure 6.

Phase separation kinetics observed in a PSAF/MMA(10/90) mixture obtained with different irradiation intensity: (a) 0.03mW/cm^2 ; (b) 0.06mW/cm^2.

characteristic length scales ξ on $(t - t_o)$ for the graded morphology observed at three positions along the Z-direction of a PSAF/MMA(10/90) mixture irradiated respectively with the intensities 0.03 and 0.06 mW/cm^2. For both intensities, the characteristic length scales exhibit a common behavior. First, ξ slowly increased with increasing irradiation time and then passed through an inflection point at a certain irradiation time. Eventually, ξ approaches a constant value and became unchanged with irradiation time. It was found that the phase separation kinetics depends strongly on the Z-coordinates of the mixtures and approximately follows the power law $\xi \sim (t - t_o)^{\alpha}$. At the early stage of irradiation, α is close to 1/3 as predicted by Lifshitz-Slyosov-Wagner 1/3-power law[5–6] For long irradiation time, α approaches unity, reflecting the hydrodynamic effects predicted by Siggia.[7] Eventually, phase separation was arrested by the cross-link networks and was terminated with a bi-continuous structure with a stationary wavelength determined by the competitions between cross-link reaction and phase separation.

It has been known for long time that polymerization of methyl methacrylate (MMA) is an autocatalytic reaction driven by the positive feedback between polymerization and the reaction heat.[8] For poly(*cross*-styrene)-*inter*-poly(*cross*-methyl methacrylate) IPNs studied in this work, it was found that photopolymerization of MMA is also an autocatalytic reaction.[9] To investigate the effects of coupling of this autocatalytic reaction to phase separation of the IPNs, the derivative of the characteristic length scale ξ with respect to the phase separation time $(t - t_o)$ was calculated and also illustrated in Figures 6. For the phase separation kinetics observed at the bottom position of the mixture irradiated with the irradiation intensity 0.03 and 0.06 mW/cm^2, there clearly exists an inflection point in the $\ln\xi$ vs. $\ln(t - t_o)$ as evidenced by the peak in the derivative $d(\ln\xi)/d(\ln[t - t_o])$ curve. On the other hand, the inflection point does not clearly appear in the "middle", particularly the "top" positions. The difference in the mobility at the top (with higher cross-link density) and at the bottom (with lower cross-link density) would reasonably explain the behavior of $d(\ln\xi)/d(\ln[t - t_o])$ observed at different positions.

This is worth noting that the phase separation behavior shown here can be only induced by irradiation with UV light. To confirm this particular behavior, a PSAF/MMA (5/95) mixture containing Lucirin TPO and EGDMA similar to those described above was irradiated until phase separation occurs. As soon as phase separation was recognized under microscope, UV light was turned off and the mixture was kept at the experimental temperature while the observation of the phase separation process was continued. It was found that without irradiation, the phase separation of the PSAF/MMA (5/95) mixture proceeded with an exponent $\alpha \sim 1/3$ which is in strong contrast with the case of continuous irradiation where $\alpha \sim 1$ was found. These results indicate that the phase separation observed in this study was driven by the polymerization reaction and was not affected by the so-called "frontal polymerization"[10–11] where the polymerization was induced by a large amount of heat produced by itself. It seems that the amount of heat generated only by the photopolymerization of MMA is not sufficient to further induce phase separation of the mixture. It would be possible if more intense light source as UV laser is used. However, these experiments are beyond the scope of our current motivation.

Concluding Remarks

In this study, a novel method for generating polymer blends with graded morphology was proposed for poly(*cross*-styrene)-*inter*-poly(*cross*-methyl methacrylate) IPNs by taking advantages of a light-intensity gradient. The resulting morphology was *in-situ* investigated by using a laser-scanning confocal microscope. The findings can be summarized as follows:

1) By irradiation with strong light, a gradient of the light intensity was produced inside the sample. Induced by this spatially non-uniform intensity, a gradient of quench depth and of mobility was generated from the top to the bottom of the mixture, leading to a spatially graded morphology. On the other hand, no graded morphology was formed upon irradiation with a weak intensity because a gradient of light intensity in the sample was almost negligible.
2) Phase separation of the mixture was accelerated by the autocatalytic polymerization reaction of methyl methacrylate monomer. The average rate of phase separation revealed a peak, indicating that phase separation was driven by the reactions in an autocatalytic fashion. This autocatalytic behavior of phase separation was significant not only in the bottom of the mixture but also in the mixture irradiated with a strong light intensity. This peculiar

autocatalytic phase separation would be attributed to the additional heat generated by the photo-polymerization reaction.

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