Phase separation kinetics and morphology induced by photopolymerization of 2-hydroxyethyl methacrylate (HEMA) in poly(ethyl acrylate)/HEMA mixtures

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Abstract

Morphology and phase separation kinetics induced by polymerization of 2-hydroxyethyl methacrylate (HEMA) in a HEMA/poly(ethyl acrylate) (PEA) mixture were observed by laser scanning confocal microscope in the presence of lucirin TPO used as an initiator. The results were analyzed by 2D-Fourier transform (2D-FFT). The photopolymerization is driven by irradiation with visible light $\lambda = 405$ nm. The mixture exhibits the Trommsdorff–Norrish effect which is responsible for a drastic increase in the reaction rate during the irradiation process. The concentration fluctuations and the increase in the viscosity of the medium play an important role in promoting the reaction yield. PHEMA droplets were found to develop in the rhodamine-B-labeled poly(ethyl acrylate) (PEA-Rh) continuous matrix. The characteristic length of the morphology increases with increasing irradiation intensity, revealing the tool to control the morphology by varying the light intensity.

Keywords: 2-hydroxyethyl methacrylate, photo-polymerization, self-acceleration, phase separation, morphology

Classification number: 4.13

1. Introduction

Poly(2-hydroxyethyl methacrylate) (PHEMA) has been a well-known polymer since the 1960s due to its wide applications in materials science, ranging from soft contact lenses, holographic applications to biomedical materials such as polymers for implants, drug delivery devices, support for enzyme immobilization, cosmetic applications and so on [1–7]. Chemical synthesis of the HEMA monomer and its derivatives, and their polymerization and copolymerization have been reviewed, together with practical applications of PHEMA [8]. Depending on the demand of the final products, attempts to improve the physical properties of PHEMA have been elaborated by modifying the hydrophobicity, the water of hydration and so on [9]. Recently, it was reported that the biological response of PHEMA can be modified and controlled by regulating the phase-separated domains of the block copolymers of HEMA and ethyl acrylate [10], greatly extending the applicability of PHEMA.

In the past decades, from the viewpoint of pattern formation driven by competing interactions [11, 12] we have utilized photo-cross-link reaction [13] and photopolymerization [14] to induce and control the morphologies of polymer mixtures undergoing phase separation. Through the competition between phase separation and polymerization, various morphologies have been produced and controlled. Since the physical properties, particular the morphology at the mixture interface, play a crucial role in applications such as controlling the
Figure 1. Chemical structure of (a) 2-hydroxyethyl methacrylate (HEMA); (b) lucirin TPO; (c) poly(ethyl acrylate) labeled with rhodamine B (PEA-Rh).

Figure 2. Photopolymerization kinetics of HEMA in situ monitored by FTIR upon irradiation with 405 nm at 25°C under various intensities.

spatial distribution of cells, the free energy at the interfaces, the flexural modulus of the materials, etc, we will show in this study that the morphology of PHEMA/PEA blends can be regulated and controlled by photopolymerization of HEMA in the mixture. First, the polymerization of ethyl acrylate monomer and the procedure of labeling PEA with rhodamine B will be described together with the information on characterization of the polymer. The detail of the photopolymerization kinetics monitored by FTIR will be compared with the phase separation kinetics obtained by laser-scanning confocal microscopy (LSCM). The effects of light intensity as well as the blend composition are discussed from the viewpoint of systems with competing interactions. Finally, the possibility of utilizing this experimental procedure to construct composites containing polymers and natural fibers will be mentioned.

2. Experimental

2.1. Sample preparation

In this study, a homogenous mixture of poly(ethyl acrylate) (PEA) and 2-hydroxyethyl methacrylate (HEMA) was used as the sample. The PEA component was labeled with a trace of rhodamine B for fluorescence imaging using laser scanning confocal microscope (LSCM). Rhodamine B labeled PEA was synthesized by copolymerization of ethyl acrylate with methyl methacrylate MMA-Rhodamine (Polysciences, Inc., used without further purification) in acetone under reflux condition and was precipitated using water as non-solvent. The detail of the synthesis is described elsewhere [15]. The weight-average molecular weight $M_w$ and the polydispersity ($M_w/M_n$) of rhodamine B-labeled poly(ethyl acrylate) (PEA-Rh) are respectively $1.6 \times 10^5$ and 2.3. In this system, in the presence of 2 wt% of Lucirin TPO as a photoinitiator, HEMA (Wako Pure Chemical Industries, Japan) undergoes polymerization upon irradiation with 405 nm visible light. The structures of these chemicals are shown in figure 1. Sample size was $20 \mu m \times 20 \mu m \times 75 \mu m$. All the experiments were carried out at room temperature (25°C).

2.2. Instruments and data analysis

2.2.1. Reaction kinetics. The polymerization kinetics of HEMA in PEA-Rh/HEMA mixture was in situ monitored during the irradiation process by using Fourier transform infrared (FTIR, Perkin-Elmer, model Spectrum GX). Irradiation at 405 nm was conducted with a high pressure mercury lamp (350 W, Moritex, Japan) equipped with a bandpass filter (Asahi Spectra Co., Ltd) to perform monochromatic radiation. The polymerization yield $\phi$ (%) was obtained from the variation with irradiation time in the absorbance of the C=C bond of HEMA monomer monitored at $1640 \text{ cm}^{-1}$ with the absorbance of the C–O bond at $1720 \text{ cm}^{-1}$ as the internal reference. The polymerization yield was defined as

$$\phi \ (%) = \left\{ \frac{(A_{C=C})_t/ (A_{C=C})_{t=0}}{(A_{C=O})_t/ (A_{C=O})_{t=0}} \right\} \times 100 \%, \quad (1)$$

where $A$ represents the absorbance of the corresponding vibrational modes observed by FTIR spectra.
2.2.2. Morphology observation using a laser scanning confocal microscope (LSCM). The photoreaction-induced morphology was observed by using laser scanning confocal microscope (LSM 5 PASCAL, inverted type, Carl Zeiss). The details of this instrument were reported elsewhere [16]. The morphology of PEA-Rh/HEMA blend was monitored during the irradiation process to observe the phase separation process. Also, the stationary morphology was observed by irradiation over 60 min. All of the morphology was analyzed by using two-dimensional fast Fourier transform (FFT) as reported previously [17]. The morphology was investigated for various compositions of PEA-Rh/HEMA blend and under various irradiation intensities.

3. Results and discussion

3.1. Polymerization kinetics of HEMA monomer in the bulk state

The photopolymerization of 2-hydroxyethyl methacrylate (HEMA) monomer was carried out by using Lucirin TPO as a photoinitiator. The polymerization yield $\phi$ (%) was calculated by using equation (1).

In figure 2, the left axis shows the polymerization yield $\phi$ (%) as a function of irradiation time under three different intensities $I = 0.025$, 0.05 and 0.5 mW cm$^{-2}$. The right axis shows the irradiation-time dependence of the mean reaction rate $d\phi/dt$ expressed by the derivative of the conversion under the same conditions. The reaction was found to significantly increase after a certain irradiation time, e.g. by 2 min of irradiation with 0.5 mW cm$^{-2}$. This is a typical example for the so-called Trommsdorff–Norrish effect which is caused by the positive feedback loop composed of increase in viscosity and suppression of the termination step of the polymerization [18, 19]. It was found that higher conversion and faster reaction rate were observed under stronger irradiation intensities. This can be explained by the fact that the molecular weight of PHEMA was reduced under irradiation with high irradiation intensity, which leads to the decrease in viscosity of the reacting media.

From figure 2, it was found that the characteristic time $\tau$ and the maximum of the mean reaction rate expressed by the peak of $(d\phi/dt)$ gradually shifts to the side of longer irradiation time, whereas the height of $(d\phi/dt)$ gradually decreases with increasing irradiation intensity. The decrease of molecular weight under higher irradiation intensity could be responsible for this phenomenon. Figure 3 shows the dependence of the characteristic time $\tau$ and the mean reaction rate $(d\phi/dt)_{max}$ on the irradiation intensity. It was found that the characteristic time $\tau$ decreases, whereas the maximum rate increases with the irradiation intensity. For intensity in the range 0.025–0.5 mW cm$^{-2}$, these above results again confirmed that the reaction rate is faster for irradiation with higher intensity.

3.2. Polymerization kinetics of HEMA in the presence of PEA-Rh

To investigate the effects of PEA-Rh on the polymerization kinetics, the polymerization yield $\phi$ (%) was measured as a function of irradiation time under three different intensities $I = 0.025$, 0.05 and 0.5 mW cm$^{-2}$ for PEA-Rh/HEMA (10/90) mixtures. Similarly, the effects of irradiation intensity on the polymerization yield and reaction rate were observed for PEA-Rh/HEMA (10/90) mixture. The results are illustrated in figure 4.
Figure 5. Intensity dependence of (a) characteristic time $\tau$ and (b) maximum polymerization rate observed for HEMA in PEA-Rh/HEMA (10/90).

Figure 6. Photopolymerization kinetics of HEMA in PEA-Rh/HEMA (0/100) and PEA-Rh/HEMA (10/90) in situ monitored by FT-IR under various irradiation intensities: (a) $I = 0.025\text{ mW cm}^{-2}$, (b) $I = 0.05$, and (c) $I = 0.5\text{ mW cm}^{-2}$.
Figure 7. Morphology obtained for PEA-Rh/HEMA (12/88) mixtures containing 2 wt% of lucirin TPO as an initiator under irradiation with various intensities at 405 nm: (a) 0.025; (b) 0.05; (c) 0.5; (d) 1.5; (e) 2.5 mW cm$^{-2}$.

The characteristic time $\tau$ and the maximum reaction rate $(d\phi/dt)_{\text{max}}$ were also analyzed and are shown in figure 5. As was found for PEA-Rh/HEMA (0/100), the characteristic time $\tau$ decreased with the irradiation intensity although the maximum reaction rate $(d\phi/dt)_{\text{max}}$ increased for the blend system with 10 wt% of PEA-Rh. The results demonstrated the influences of the autocatalytic feedback, concentration fluctuation [20] and change in viscosity on reaction kinetics of a polymer blend.

3.3. Comparison between the polymerization kinetics of HEMA in a mixture with and without PEA-Rh under various irradiation intensities

The polymerization kinetics of HEMA in PEA-Rh/HEMA (0/100) and PEA-Rh/HEMA (10/90) is compared in figure 6 under three different irradiation intensities $I = 0.025, 0.05$ and 0.5 mW cm$^{-2}$. As shown in figure 6(a), the difference in the polymerization yield becomes more significant when the sample was irradiated under lower
intensity $I = 0.025 \text{ mW cm}^{-2}$. An amount of 10 wt% of PEA-Rh was found to enhance the polymerization yield of HEMA. This result can be explained as follows: in the presence of PEA-Rh, the concentration fluctuation increases, leading to the condensation of HEMA monomer in the PEA-Rh-rich region because the Hildebrand solution parameter $\delta$ of HEMA monomer is closer to PEA-Rh compared to PHEMA ($\delta_{\text{HEMA}} = 12.19$ [21], $\delta_{\text{PEA}} = 18.27$ [22] and $\delta_{\text{PHEMA}} = 26.93$ [23, 24]). As a result, the reaction yield of HEMA increased when PEA-Rh was added into the mixture. On the other hand, the distinction in the reaction yield for PEA-Rh/HEMA (0/100) and PEA-Rh/HEMA (10/90) is less when the irradiation intensity increases to 0.05 and 0.5 mW cm$^{-2}$ (figures 6(b), 6(c)).

As mentioned above, when the intensity increases, the viscosity of the solution decreases due to the reduction of PHEMA molecular weight. Consequently, the concentration fluctuation decreases and the difference in the reaction yield is less.

### 3.4. Phase separation kinetics observed for PEA-Rh/HEMA mixture

Irradiation with $\lambda = 405 \text{ nm}$ triggers photopolymerization of HEMA in the presence of lucirin TPO. As the fraction of PHEMA networks exceeds a critical threshold, phase separation takes place. During the irradiation process, the viscosity of the mixture continues increasing until the whole system becomes glassified. At that stage, the stationary morphology is obtained. Figure 7 displays the fluorescence micrographs of the stationary morphologies obtained for PEA-Rh/HEMA (12/88) under various irradiation intensities. The red (bright) region in the micrographs represents the PEA-Rh-rich phase as imaged by the fluorescence of rhodamine B, whereas the nonfluorescent black domains correspond to the PHEMA-rich phase. The corresponding two-dimensional (2D) fast Fourier transform (FFT) power spectrum are illustrated for each micrograph. Small droplets of PHEMA grow quickly in the continuous phase of PEA-Rh under irradiation. The PHEMA droplets become larger with irradiation intensity. The three dimensional (3D) morphology obtained after 60 min of irradiation with $\lambda = 405 \text{ nm}$ visible light is displayed in figure 8.

For further discussion, the characteristic length of the morphology ($\xi$) observed for PEA-Rh/HEMA mixture with different compositions was analyzed and is shown in figure 9. It was found that these results share a common behavior for intensity-dependence of the characteristic length $\xi$. For a given composition, $\xi$ increases with increasing irradiation intensity. The experimental results seemingly contradict what was reported for photoreaction-induced phase separation of polystyrene/methyl methacrylate mixtures [16]. It was reported for spinodal decomposition process that the characteristic length $\xi$ decreases when the irradiation intensity increases because of the high crosslink density [25].

As described above, the polymerization of HEMA is very fast under irradiation with $\lambda = 405 \text{ nm}$ visible light, the
reaction quickly approaches the characteristic time $\tau$, e.g. for a PEA-Rh/HEMA (10/90) mixture irradiated under $I = 0.025 \text{ mW cm}^{-2}$, $\tau$ is about 7 min. Nakanishi et al [26] reported that the irradiation time at which the droplet size reaches the stationary state corresponds well to the time where the rate of polymerization of methyl methacrylate (MMA) reaches its maximum. Because the polymerization is too fast for this particular case, it is difficult to detect the growth of the droplets during the time required to achieve the stationary state of phase separation process. It is believed that the difference between the behavior of the phase separation in these two cases is driven by two different mechanisms: spinodal decomposition (e.g. for polystyrene/methyl methacrylate blends) and nucleation-and-growth (e.g. PEA-Rh/HEMA blends).

Moreover, in order to understand the effects of the composition on the characteristic length of the obtained morphology, the characteristic length $\xi$ is plotted versus the weight fraction of PEA-Rh in figure 10 for two different irradiation intensities $I = 0.05$ and $0.5 \text{ mW cm}^{-2}$. It was found that $\xi$ decreases when the weight fraction of PEA-Rh increases. The behavior could be explained by the increase in the viscosity of the medium when weight fraction of PEA-Rh increases.

4. Conclusions

In this paper, we have reported the kinetics and the morphology observed during the phase separation process of a PEA-Rh/HEMA blend with different compositions under various irradiation intensities. The following results were obtained:

1. The kinetics of photopolymerization of HEMA in solution with 2 wt% of lucirin TPO was examined by FTIR spectroscopy. It was found that the autocatalytic feedback enhanced the reaction rate significantly. In addition, the reaction yield increased with the stronger irradiation due to the diminishment in the molecular weight of the generated PHEMA, leading to the decrease in viscosity.

2. In the presence of PEA-Rh, the reaction yield increases due to the concentration fluctuations of the two components in the systems.

3. By using LSCM, the morphology induced by photopolymerization of HEMA in PEA-Rh/HEMA was observed. The results obtained for several compositions of PEA-Rh/HEMA blend show that the characteristic length of the structure increased with increasing irradiation intensity, suggesting that light can be used to generate and control the length scales of the morphology of polymer mixtures. These data would provide a way to design various polymer templates useful for nanoparticle dispersion.

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