

Phase Separation in Reacting Soft Matter (I) :

Formation of Co-continuous Structures with Spatial Gradients

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<概要>

相溶しているポリマーブレンドは温度や圧力、また化学反応によって熱力学的に不安定になり、相分離が誘発される。本研究室では、光架橋反応と光重合反応との競合を利用することによって相分離を定量的に誘発・制御してきた。ここでは同一試料内において空間的に非一様な反応を引き起こし相分離過程に及ぼす影響について検討することを目的とする。

Introduction

The stability of a mixture under thermodynamic equilibrium conditions is dictated by Gibbs free-energy minimum. The purpose of this study is to induce and control phase separation of polymer mixtures undergoing phase separation under conditions far-from-equilibrium. These conditions can be realized by using a temperature gradient to induce phase separation of a polymer blend[1,2]. However, the temperature used to induce phase separation is interfered by the temperature of the phase diagram and is therefore cannot provide an efficient way to control the gradient of the free-energy of the polymer blend. As a consequence, we use light intensity gradient to induce phase separation. Under these specific conditions, a spatial gradient of the Flory's χ parameter was generated and controlled along the propagation direction of the exciting UV light, leading to the formation of a variable gradient of the quench depth. Phase separation kinetics and morphology of polymer blends under these particular conditions were examined and discussed.

Samples used in this work are homogeneous mixtures containing anthracene-labeled polystyrene(PSA) and methylmethacrylate(MMA) monomer. Irradiation with 365nm UV light produces PSA networks via photodimerization of anthracene moieties on the PSA chains. Appropriate photo-initiator and photo-cross-linker were also dissolved in the mixture to provide a tool to generate PMMA networks under irradiation. By this particular chemical design, irradiation can simultaneously generated both PSA and PMMA chains. The graded spinodal structures of these IPNs were observed *in situ* under a laser confocal scanning microscope (LCSM, Pascal LSM, Zeiss). To enhance the contrast of the morphology of these IPNs, fluorescein was also chemically labeled on PSA chains. The 3-dimensional structures of phase-separated IPNs was constructed by using conventional software.

Results and Discussion

Upon irradiation with a weak UV intensity ($0.01\text{mW}/\text{cm}^2$), spatially uniform co-continuous morphology emerges. However, as the light intensity increases to $0.06\text{mW}/\text{cm}^2$ the spinodal structure becomes spatially graded. An example is shown in Figure 1 where the morphology

emerging at different depth is displayed for the same sample. Obviously, the spinodal structures with a gradient of characteristic length scale ξ were observed. As shown in Figure 2, ξ increases with increasing irradiation time and eventually approaches a stationary value which depends on the depth of the sample. These results indicate that these graded spinodal structures induced by the gradient of light intensity can be frozen at long irradiation time and the blend eventually becomes a polymeric materials with graded periodic structure determined by the incident light intensity. This graded morphology can be controlled by changing the incident light intensity as shown in Fig. 3 where the gradient of the characteristic length scale of the spinodal structures in the sample greatly changes with the light intensity. Further analysis of these graded spinodal structures is currently in progress and the results will be presented at the Poster Session.

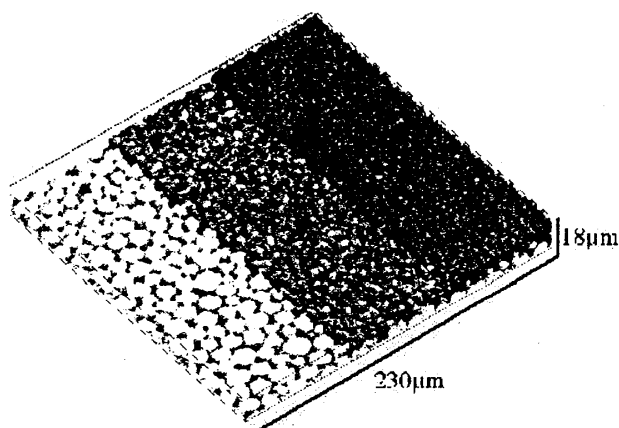


Fig.1 3-Dimensional structure of graded co-continuous structure obtained with the light intensity 0.03mW/cm^2 .

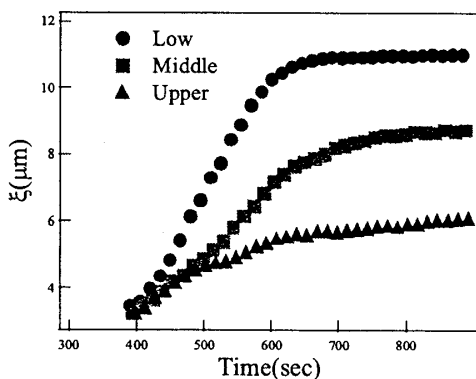


Fig.2 Time development of the characteristic length scale observed under various depths at 0.03mW/cm^2 light intensity.

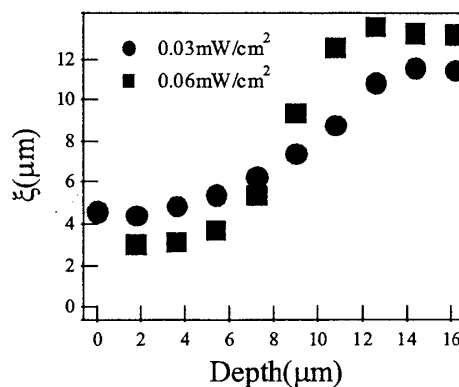


Fig.3 Irradiation intensity dependences of characteristic length scale.

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References

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