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Study on Structure Development of Polymer Blends under the Continuous Change of Quench Depth

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Contents

Chapter 1.

General Introduction

Phase separation is an important problem in the practical application of polymeric materials comprising polymer alloys and polymer blends. These materials undergo several types of phase separation, *i.e.*, micro- and macro- phase separation, phase separation via nucleation and growth, and phase separation via spinodal decomposition (SD). By controlling the morphology of the domains generated during phase separation, the typical properties of these polymeric materials, such as their mechanical properties, can be determined [1-2]. Therefore, understanding the mechanisms of phase separation and domain formation is important for the further development of such polymeric materials.

In polymer alloys, many combinations of dissimilar polymers have been observed to have phase diagrams, *i.e.*, the polymers are miscible within limited temperature and composition ranges but are immiscible outside these ranges. When a miscible polymer mixture is subjected to a rapid temperature change in the immiscible region and annealed isothermally, demixing occurs via SD in many cases, yielding a highly interconnected two-phase morphology with a unique periodicity.

For material design, the SD induced by chemical reactions is more interesting. This behavior is typically illustrated by the polymerization of monomer A in the presence of polymer B [3-14]. For example, poly(ether sulfone) (PES) is soluble in an epoxy monomer, and a PES/epoxy mixture has a lower critical solution temperature (LCST)-type phase diagram. This initially miscible system, however is thrust into the immiscible region because of the depression in the LCST due to the increasing molecular weight as the curing reaction proceeds [4]. Phase separation thus occurs via SD. Reaction-induced SD yields a variety of two-phase structures, including interconnected globule structures, isolated domain structures with uniform domain sizes, and bimodal domain structures, depending on the relative rates of the chemical reaction and phase separation.

In chapter 2, a similar situation was confirmed for the radical polymerization of methyl methacrylate (MMA) in the presence of poly(ethylene-*co*-vinyl acetate). As the polymerization of MMA proceeded, phase separation occurred via SD induced by the increase in the quantity of the polymer (PMMA). This conclusion was supported by a characteristic change in the light-scattering profile with polymerization time and the appearance of a modulated structure in the early stage of phase separation, as observed using an optical microscope. The change in the light-scattering profile during this phase separation was different from that observed during conventional SD with an isoquench depth, in which the periodic distance remains constant in the intermediate stage of phase separation. SD driven by chemical reactions proceeds isothermally; however, the quench depth ΔT, which is the temperature difference between the LCST and reaction temperature, increases with time. On the other hand, conventional SD proceeds with the isoquench depth. For phase separations induced by chemical reactions, time variations in the light-scattering profiles of the reaction mixtures and various final morphologies have been observed. In many cases, structure coarsening is suppressed during demixing.

In chapter 3, we selected a binary mixture of polystyrene and poly (vinyl methyl ether) having the lower critical solution temperature (LCST) in order to verify the influence of the successive increase of quench depth to phase separation and we carried out light scattering studies in this system under the successive increase in the thermodynamic quench by the continuous increase of temperature with time.

In chapter 4, we selected two binary mixtures; an epoxy/polystyrene (PS) system (monomer A/polymer B) comprising a linear epoxy polymer obtained via simple polymerization, such as curing of an acid anhydride and an epoxy monomer, and an epoxy/epoxy system (monomer A/monomer B) with a simple phase diagram for a symmetrical mixture. Light-scattering analysis of the epoxy/PS system and ultra-small-angle X-ray scattering (USAXS) analysis of the epoxy/epoxy system, which had a very short periodic phase separation distance, were performed.

Computer simulation of the growth of a concentration fluctuation is based on the Cahn–Hilliard nonlinear diffusion equation [8]. In this simulation, a homogeneous system is initially allowed to demix isothermally for a while at a shallow quench, and then the mixed system experiences a continual increase in the quench depth at a constant rate. With a rapidly increasing quench depth (6 °C/s), the initial concentration profile is preserved for a period of time and then it becomes rectangular, while the periodic distance and amplitude of the initial fluctuation are maintained even at the largest quench depth. On the other hand, with a slowly increasing quench depth (3 °C/s), the initial concentration profile rapidly becomes rather rectangular as the quench depth increases, but the periodic distance remains constant. A rapid growth of the concentration fluctuation with a shorter periodic distance then appears and overlaps the previous one.

There have been several theoretical attempts to investigate the phase separation processes under chemical reactions by using the time-dependent Ginzburg–Landau (TDGL) model with simple chemical reactions of low-molecular-weight materials [15-16]. Additionally, a few attempts have been made to extend the TDGL model to complex polymeric systems during polymerization. However, few of these studies were performed using the dynamic self-consistent field (SCF) theory [17-18]. With the dynamic SCF theory, it is possible to consider the molecular architectures and conformations of the constituent polymer chains using path-integral calculations.

In chapter 5, computer simulations of the phase separation of these systems as the thermodynamic quench continually increased using the OCTA [19] multi-scale modeling method for polymeric materials were also performed.

Chapter 2.

Polymerization-Induced Spinodal Decomposition of Poly(ethylene-*co*-vinyl acetate) / Methyl Methacrylate Mixture

Introduction

The spinodal decomposition induced by polymerization is typically demonstrated in an epoxy / poly(ether sulfone) system with a LCST (lower critical solution temperature)-type phase diagram. The binary mixture is homogeneous at curing temperature (below LCST). When the cure reaction proceeds, the system is thrust into a two-phase regime by the LCST depression caused by molecular weight increase and phase separation takes place via spinodal decomposition [1]. The reaction-induced spinodal decomposition yields a variety of two-phase structures: interconnected globule structure, isolated domain structure with uniform domain size, and bimodal domain structure, depending on the relative rates of the chemical reaction and the phase separation [1-3]. In such thermoset/thermoplastic systems, the chemical reactions that occur during curing are very complicated. They may involve chain extension, branching, and cross-linking, and these reactions cause a change in the physical state of the mixture.In this chapter, we deal with a simpler system: the radical polymerization of methyl methacrylate (MMA) in the presence of poly(ethylene-*co*-vinyl acetate) (EVA). In this system, the reaction is only the polymerization of MMA to form poly(methyl methacrylate) (PMMA). We investigate polymerization-induced spinodal decomposition by time-resolved light scattering and discuss it on the basis of current understanding of spinodal decomposition.

Experimental

Poly(ethylene-*co*-vinyl acetate) (EVA) was supplied by Mitsui-du Pont Chemical Co. (EV-45LX; 46wt% vinyl acetate content, $M_n = 2.75 \times 10^5$, $M_w / M_n = 1.9$ by gas permeation chromatography (g.p.c)). Methyl methacrylate (MMA) and an initiator, α,α'-azobis(isobutyronitrile) (AIBN), were commercial products. They were used without further purification. EVA and AIBN were dissolved in MMA to make up a 20/80/0.2 (by weight) EVA/MMA/AIBN mixture. Figure 2.l(a) shows the sample cell prepared by pouring this monomer syrup into the glass cell and sealing it. The sample cell was placed in a hot chamber, set horizontally on the light-scattering stage as shown in Figure 2.l(b). The hot chamber was set at 80°C. The radiation of a He-Ne gas laser beam of 632.8 nm wavelength was applied vertically to the sample cell. A goniometer trace of the intensity of scattered light was obtained under a Vv (parallel polarized) optical alignment. Thus, the change of the light-scattering profile was observed during the polymerization process. The scattering angle θ within the sample is related to the observed scattering angle, θ_{obs}, by

$$n \sin\theta = \sin\theta_{obs} \tag{2.1}$$

where n is the refractive index of the sample. The intensity of scattered light was corrected by multiplying by C_n:

$$C_n = n^2 \cos\theta / \left(1 - n^2 \sin^2\theta\right)^{1/2} \tag{2.2}$$

A light-scattering pattern was also taken by the photographic technique used by Stein and Rhodes [4].

The phase diagram of the MMA/EVA/PMMA ternary solution was measured by the cloud point method: a transparent mixture in a glass tube at an elevated temperature (80°C) was rapidly quenched to various temperatures and the change in turbidity with time was examined for 15min by the naked eye. The cloud points thus measured had accuracy of ± 1 °C. The PMMA used in this experiment was synthesized by bulk polymerization at 80°C, and its M_w and M_w / M_n by g.p.c were 5.86 x 10^5 and 1.82 respectively. An inhibitor, *p*-*tert*-butylcatechol (0.1 wt%), was added to the ternary solution to prevent thermal polymerization of MMA during cloud point measurement.

MMA conversion was measured by differential scanning calorimetry (d.s.c)(DuPont 9000 Thermal Analyzer).

Results and Discussion

Phase behavior

Cloud point curves of PMMA/EVA/MMA ternary mixtures are shown in Figure 2.2, where m_0 indicates the weight fraction of MMA. Upper critical solution temperature (UCST)-type phase behavior is seen. From these cloud point curves, one can draw a triangular phase diagram at a fixed temperature. In Figure 2.3 is shown the diagram at 80 °C. There is a small single-phase region in the diagram. Since the EVA content was fixed at 20wt%, the polymerization process can be described by the arrow in Figure 2.3. From the time-conversion curves at 80°C (Figure 2.4), the time variation of composition is shown by solid circles on the curve. In the triangular phase diagram, one can see that the system will be thrust into the two-phase regime when the polymerization proceeds to ca. 2wt% conversion level.

Morphology formation

Under the microscope, the system was homogeneous just after a temperature jump from room temperature to the polymerization temperature (80 °C). After a certain time lag, two-phase structure with low contrast appeared and the contrast became higher with polymerization time. In this time range, a ring pattern of the scattered light was detected and it became brighter with time, and then the ring diameter detected at the late stage of polymerization. Figure 2.5 shows a typical optical micrograph and light scattering pattern of the specimen polymerized for 2 h. The micrograph clearly shows the uniform interdomain spacing and uniform domain size. It is consistent with the ring pattern. The regularly phase-separated structure is quite similar to that by isothermal spinodal decomposition. Figure 2.6 shows a SEM micrograph of 80 / 20 PMMA/EVA system after polymerization at

90°C for 24h. The bi-continuous nature is lost but the regularity is still maintained. Most interesting is that PMMA (major) phase is not the matrix but the dispersed phase. That is, PMMA particles are dispersed in spite of a much greater amount of PMMA than EVA. Such two-phase structure can't be formed by the simple melt-blending, by which the major component usually tends to be the matrix. A plausible scenario for this unique two-phase structure may be as follows. After the temperature jump to the polymerization, the homogeneous mixture starts to phase separate by spinodal decomposition, such as schematically shown in Figure 2.7. In the beginning of phase separation (A), amount of PMMA-rich phase is less than EVA-rich phase from the principle of lever as shown in Figure 2.7, because the ternary system will be thrust into the two-phase regime when the polymerization proceeds to ca. 2wt% conversion level. Namely, phase separation take place at low conversion. In this case, PMMA-rich phase was minor phase, then continuous nature of PMMA-rich phase was lost, and the morphology was fixed by vitrification of PMMA-rich phase. So PMMA-rich phase is the dispersed phase because the final spherical domain structure may be produced by the interruption of a co-continuous percolation structure.

The time-resolved light-scattering profiles are shown in Figure 2.8, where q is the scattering vector defined by

$$q = (4\pi/\lambda)\sin(\theta/2) \tag{2.3}$$

where λ is the wavelength of light in the specimen. A peak in the light-scattering profile appears after about 5 min and then increases continuously with time. Note that the peak position does not change up to 20 min. After the peak reaches a maximum, the peak position starts to shift toward a smaller angle as the polymerization progresses further. The peak shift continues up to 30 min and then the profile becomes invariant. From the peak angle q_m is calculated by equation

2.3. In Figure 2.9 q_m is plotted as a function of reaction time t. The intensity at q_m, I_m, is similarly plotted in Figure 2.9. It is interesting that the q_m value remains constant for a very long time. Combining the results in Figures 2.9 and 2.4 one can see that concentration fluctuation develops a periodic nature at ca. 2% conversion of MMA, the periodic distance ($2\pi / q_m$) remains essentially constant for a while (up to about 18% conversion) and then starts to increase, i.e. the structure coarsening proceeds; eventually the coarsening stops at 80% conversion.

Analysis by the linearized theory

It is interesting to check the applicability of the linearized theory of SD to the early stage of the reaction-induced SD. In the linearized theory the scattering intensity I grows exponentially

$$I(q,t) = I(q,0)\exp[2R(q)t] \tag{2.4}$$

where $R(q)$ is the amplification factor representing the growth rate of concentration fluctuation with q. $R(q)$ is described by

$$R(q) = -Mq^2\left(\frac{\partial^2 f}{\partial c^2} + 2\kappa q^2\right) \tag{2.5}$$

where M is a translational diffusion constant, f is the free energy density of a homogeneous system at composition c, and κ is an energy gradient coefficient. Logarithmic plots of $I(q,t)$ at some selected wavenumbers are shown in Figure 2.1 0. At the early stage ($t < 8$ min), the linear regime is observed for all values of q. Note that, even after the deviation from linearity begins at $t > 8$ min, $q_m(t)$ still remains constant. This could be a very characteristic feature of SD induced by polymerization. A plausible interpretation for this strange time variation of q_m may be as follows. From the linearized theory in the early stage, q_m is given by [5]

$$q_m \sim |\chi - \chi_s|^{1/2} \sim |T - T_s|^{1/2} \tag{2.6}$$

Large quench depth results in large q_m. As shown in Figure 2.2, the quench depth is expected to increase continuously with polymerization of MMA. Therefore the polymerization may course a shift to large q_m. This continuous increasing of the quench depth causes the predominance of large q_m. On the contrary, the phase-separated structure should be coarsened by the interfacial instability to make q_m smaller. The constant q_m may be due to the balance of both thermodynamic driving forces. Namely it is considered that the coarsening is suppressed by the increase in the quench depth. Using the values of $R(q)$ determined from the slopes of straight lines in the linear regime, the plot of $R(q) / q^2$ versus q^2 is given in Figure 2.11. As expected from equation 2.5, fairly straight lines are shown. The apparent diffusion coefficient, D_{app}, defined by

$$D_{app} = M \frac{\partial^2 f}{\partial c^2} \tag{2.7}$$

and critical wavenumber $q_m(0)$ were obtained from intercepts on the x and y axes in Figure 2.11. Results are summarized in Table 2.1. Note that the above analyses are based on implicit assumptions: M, κ and $f(c)$ are constant (being independent of time). In general, these assumptions could not be satisfied in the reactive systems. However, the linear relationships in Figures 2.10 and 2.11 may suggest that the assumptions are approximately true in the very early stage of the reaction induced spinodal decomposition.

Table 2.1 Kinetic parameters describing the polymerization-induced SD

$-D_{app} \times 10^{12}$ ($\mathrm{cm^2 s^{-1}}$)	$q_m(0)$ ($\mu\mathrm{m}^{-1}$)	α	β	$\Delta\Lambda_m / \Delta t$ ($\mu\mathrm{m\ min^{-1}}$)
2.7	4.74	1.07	2.68	0.104

Scaling analysis for the late stage

The decrease in $q_m(t)$ accompanied by the increase in $I_m(t)$ with time at the late stage in Figure 2.9 indicates the occurrence of coarsening. Time evolution of $q_m(t)$ and $I_m(t)$ is expressed by the power law:

$$q_m(t) = t^{-\alpha} \tag{2.8}$$

$$I_m(t) = t^{\beta} \tag{2.9}$$

The exponents α and β have been calculated for the SD in a simple binary system by many researchers. Langer, Baron and Miller (LBM) obtained the value of $\alpha = 0.21$ on the basis of non-linear statistical considerations [6]. Binder and Stauffer [7] considered the coalescence of cluster domains to get the values $\alpha = 1 / 3$ and $\beta = 1$. Lifshitz and Slyozov also predicted $\alpha = 1 / 3$ for solid mixtures according to the vaporization-condensation mechanism [8]. Siggia obtained $\alpha = 1 / 3$ for the early stage and $\alpha = 1\ 1$ for the intermediate stage (flow stage) by taking account of diffusion and hydrodynamic flow [9]. Thus various values for $\underline{\alpha}$ and β have been reported depending on the coarsening mechanism. The exponents obtained from the slopes in the straight regime at the late stage, e.g. after about 20 min in Figure 2.9 are listed in Table 2.1. The values are close to those given by Siggia. This may imply that a percolation structure is initially formed and then transformed into clusters as seen in the final structure in Figure 2.9. It should be noted that this conclusion is only phenomenological, since in the reaction-induced SD many physical constants may change with time so that the basic assumptions might be violated.

In order to characterize the change of the phase-separated structure during polymerization, the time evolution of the scaled structure function was also investigated. Time evolution of a scattering profile $I(q, t)$ is expressed by [10]

$$I(q,t) \sim \left\langle \eta^2 \right\rangle q_m(t)^{-3} S(q(t)/q_m(t)) \tag{2.10}$$

where $S(q(t)/q_m(t))$ is the structure function, and $<\eta^2>$ is the mean-square fluctuation for the spatial variation of scattering contrast [11]:

$$\langle \eta^2 \rangle \sim \phi_1\phi_2(p_1 - p_2)^2 \qquad (2.11)$$

ϕ_i and p_i indicate the volume fraction and the polarizability of phase i, respectively. Then the experimental scaled structure function is obtained by

$$F(X,t) = q_m(t)^3 I(q,t) \qquad (2.12)$$

with $X = q(t) / q_m(t)$. From equations 2.10 and 2.12, $F(X,t)$ is related to $S(X)$ by

$$F(X,t) \sim \langle \eta^2 \rangle S(X) \qquad (2.13)$$

Furukawa [12] proposed the scaled structure function as

$$S(X) = \frac{X^2}{r/2 + X^{2+r}} \qquad (2.14)$$

and pointed out that

$r = d + 1$ for cluster regime

and $r = 2d$ for percolation regime

where d is the dimensionality of the system.

Figure 2.12 show the time variation of $F(X, t)$ calculated from the result in Figure 2.8. Up to 20 min, $F(X, t)$ increases continuously with time. This seems to be due primarily to the increase in composition difference between two phases; $F(X, t)$ sharpens with time, indicating the formation of a better defined structure. When $t > 20$ min, $F(X, t)$ decreases in intensity, and becomes broader continuously with time. This implies that the structure factor $S(X, t)$ broadens during this stage. The decrease of $F(X, t)$ with time might be derived from the decrease of $<\eta^2>$ and/or the broadening of $S(X, t)$ [13]. In equation 2.11 $\phi_1\phi_2$ has a maximum value when $\phi_1 = \phi_2 = 0.5$; i.e. the larger the deviation from the symmetry, the smaller is the product of $\phi_1\phi_2$. When the system reaches ~ 20 wt% conversion, ϕ_1 and ϕ_2 could be approximately equal and further polymerization would lead the deviation from symmetry of composition (see Figure 2.3). Thus a decrease of $<\eta^2>$ with time will occur when the decrease of $\phi_1\phi_2$ prevails over the increase of $(p_1 - p_2)^2$. In Figure 2.11 are shown the double logarithmic plots of the reduced scaled structure function $F(X, t) = F(X, t) / F(l, t)$ for $t = 20$ min and $t = 32$ min. A slope of the plot for $t = 20$ min in the X range, $1.4 < X < 1.6$ is approximated by $F(X, t) \sim X^{-6}$. According to equation 2.14, this slope is expected for bi-continuous percolated networks. On the other hand, $F(X, t)$ for $t = 32$ min is described by $F(X, t) \sim X^{-4}$ (for $1.4 < X < 1.6$) reflecting the cluster structure and $F(X, t) \sim X^{-4}$ (for $X > 2.2$) suggesting the Porod's regime. Thus one can see that the broadening of the structure factor at $t > 20$ min is associated with the transformation from a percolation to a cluster structure.

Conclusion

We have found that the phase separation during polymerization of MMA in the presence of EVA can be interpreted in terms of a phase separation scheme based on SD, which is induced by the increasing of PMMA content in the mixture. This phase separation behavior is different from the ordinary isothermal SD. The final phase-separation structure may be formed by interruption of a co-continuous percolation structure to the cluster structure.

Chapter 3.

Dynamics in Spinodal Decomposition in a Mixture of Polystyrene and Poly(vinyl methyl ether) under the Continuous Change of Quench Depth

Introduction

The kinetics of phase separation of polymer solutions and mixtures quenched in an immiscible region has been investigated by the theory, the experiment and computer simulations [1-5]. However, considerable attention has been paid to isothermal (iso-quench) spinodal decomposition in polymer blends; *i. e*. the study of spinodal decomposition induced by a temperature jump from a miscible region to an immiscible region is now an interesting subject in polymer physics in terms of the order-disorder transition. Recently, it is important for producing practical materials that the study of the phase separation process accompanied with the chemical reaction.

In chapter 2, we discussed with the polymerization-induced spinodal decomposition of Poly(ethylene-*co*-vinyl acetate) / Methylemethacrylate (MMA) mixture. As the polymerization of MMA proceeded, phase separation took place through spinodal decomposition (SD) induced by the increase of the amount of polymer (PMMA). The change in light scattering profile during this phase separation is different from that of isothermal (isoquench depth) phase separation; q_m remains almost constant in the intermediate stage of phase separation. This could be caused by successive increase of quench depth accompanied with polymerization.

In this chapter, we selected a binary mixture of polystyrene and poly (vinyl methyl ether) having the lower critical solution temperature (LCST) in order to verify the influence of the successive increase of quench depth to phase separation and we carried out light scattering studies on the phase decomposition in this system under the successive increase in the thermodynamic quench by the continuous increase of temperature with time.

Conclusion

We have found that the phase separation behavior under the continuous change of quench depth is different from the ordinary isothermal quench depth in the following points: (i) For the continuous change of quench depth there is much time (reduced parameter τ defined by parameters characterizing the early stage of SD) until arising the observable fluctuation; and (ii) after growing fluctuation $Q_m(\tau)$ is slowly decreasing with τ.

Chapter 4.

Structure Development by Reaction-Induced Phase Separation in Polymer Mixtures: Analysis of Early and Late Stage Demixing

Introduction

For material design, more interesting is the spinodal decomposition induced by chemical reaction. This is typically illustrated by the polymerization of monomer A in the presence of polymer B [1-15]. For example, poly(ether sulfone) (PES) is soluble in epoxy monomer and the PES / epoxy mixture, having a lower critical solution temperature (LCST) type phase diagram, was initially a miscible system at the cured temperature; however, the system will be thrust into the immiscible region the cure reaction proceed [2]. When the cure reaction proceeds, the system is thrust into immiscible region by the LCST depression caused by an increasing molecular weight and phase separation then takes place via spinodal decomposition. Reaction-induced spinodal decomposition yields a variety of two-phase structure *i.e.*, interconnected globule structures, isolated domain structures with uniform domain size, and bimodal domain structure, depending on the relative rates of the chemical reaction and phase separation. Furthermore, dynamics of phase separation in a polymerization system, consisting of carboxyl terminated polybutadiene acryronitrile/epoxy/methylene dianiline, was investigated using a light-scattering technique [9]. In the system, the initial periodic distance was found to decrease of the chemical reaction. This peculiar kinetics of phase separation was ascribed to the nucleation-initiated spinodal process arising from the change of the phase diagram with a curing reaction. In addition, phase separation driven by a photo-cross-linking reaction was investigated by using anthracene-labeled polystyrene/poly(vinyl methyl ether) blends [14]. Upon irradiation with 365 nm ultraviolet light, anthracene moieties undergo photodimerization, leading to phase separation of the two polymers. Unlike the conventional kinetics of phase separation in non-reacting mixtures, it was found that the periodic distance was decrease as the local shrinkage in the cross-linking reaction.

In such thermoset / thermoplastic systems, the chemical reaction which occurs during curing is very complicated. It may involve chain extension, branching and cross-linking. That is, the complex chemical reaction causes a change in the physical state of the mixture. A similar situation was confirmed for the radical polymerization of methyl methacrylate (MMA) in the presence of poly(ethylene-*co*-vinyl acetate) [7]. As the polymerization of MMA proceeded, phase separation took place through spinodal decomposition induced by the increase of the amount of polymer (PMMA). This was supported by the characteristic change in the light scattering profile with polymerizing time and the appearance of the modulated structure in the early stage of phase separation from observation of the optical microscope. The change in light scattering profile during this phase separation is different from that of the familiar spinodal decomposition under iso-quench depth; the periodic distance remains almost constant in the intermediate stage of phase separation. In the phase separation induced by chemical reactions, time variations in light-scattering profiles and various final morphologies have been observed. In many cases, structure coarsening is suppressed during demixing. Spinodal decomposition driven by reaction proceeds isothermally but the quench depth ΔT, in terms of the temperature difference between LCST (or an upper critical solution temperature (UCST)) and the reaction temperature, increase with time. It is under a successive increase in quench depth. This situation is different from the familiar spinodal decomposition under iso-quench depth.

In this chapter, in order to verify the influence of the successive increase of quench depth to phase separation, we selected two binary mixtures; epoxy / polystyrene system (monomer A / polymer B), having a linear epoxy polymer by a simple polymerization such as curing of an acid anhydride and an epoxy monomer, and epoxy / epoxy system (monomer A / monomer B), having a simple phase diagram of a symmetric mixture. We carried out light scattering in epoxy / polystyrene system and ultra-small-angle X-ray scattering (USAXS) in epoxy / epoxy system, having a very short periodic distance of phase separation, on the phase separation in these systems under the successive increase in the thermodynamic quench.

Experimental

Materials

For the epoxy/PS system, the mono epoxy monomer glycidyl phenyl ether, a curing agent (3 or 4-methyl-hexahydrophthalic anhydride), and commercial PS (Aldrich Chemical Co., M_w = 90000) were used. To obtain a homogeneous mixture, the epoxy/PS mixture was prepared in a two-step process; PS was first dissolved in the epoxy monomer at 50 °C, and then the curing agent was added at room temperature. The curing agent was used at a stoichiometric ratio with the epoxy based on the hydrophthalic groups.

For the epoxy/epoxy system, two classical epoxy monomers, diglycidyl aminophenol and diglycidyl ether of bisphenol A, and the curing agent 4,4′-diamino diphenylsulfone (DDS) were used. To obtain a homogeneous mixture, the epoxy/epoxy mixture was prepared using a two-step process; the diglycidyl ether of bisphenol A was first dissolved in the diglycidyl aminophenol at 50 °C, and then the curing agent was added at room temperature. The curing agent was used at a stoichiometric ratio with the epoxy based on the amino groups. Each epoxy monomer was cured individually by the curing agent.

Technique

The light-scattering profiles of the epoxy/PS = 95/5 blend were monitored during the curing process using a light-scattering photometer (Dyna-3000, Otsuka Electronics, Japan). The sample, which was fixed between two glass slides, was set in a hot stage placed horizontally on the light-scattering stage. Radiation (632.8 nm) from a He–Ne gas laser was then applied vertically to the sample. The hot stage was programmed for a linear rise in temperature using a Linkam TH600 heating–cooling stage. The light-scattering profiles were monitored using a charge-coupled device (CCD) camera, which provided access to the scattering intensity at angles ranging from −20 to +20 degrees. The two-dimensional (2D) distribution of the light-scattering intensity was circularly averaged to obtain one-dimensional scattering intensity data. The scattering vector q is defined as follows:

$$q = \frac{4\pi}{\lambda}\sin\frac{\theta}{2}, \qquad (4.1)$$

where λ and θ are the wavelength of the incident light beam and the scattering angle in the medium, respectively.

USAXS was performed to follow the epoxy/epoxy blend on the several hundred nanometer scale. With this method, the scattering intensity depends on the heterogeneity of the electronic density and the size of the heterogeneous structure. The scattering vector q is defined as follows:

$$q = \frac{4\pi}{\lambda}\sin\frac{\theta}{2}, \qquad (4.2)$$

where λ and θ are the wavelength of the incident X-ray beam and the scattering angle in the medium, respectively.

The USAXS analyses were performed on the BL03XU frontier soft material beamline at the third-generation synchrotron facility (SPring-8). USAXS profiles of the epoxy(diglycidyl aminophenol)/epoxy(diglycidyl ether of bisphenol A) = 50/50 blend were monitored during the curing process using a 2D X-ray image intensifier with a cooled CCD (Hamamatsu Photonics, Japan, V7739P+ORCA R2). The sample-to-detector distance was 7.7 m, and the X-ray wavelength was 0.22 nm. The sample, which was fixed between two thin polyimide films, was placed in a hot stage that was positioned vertically on the USAXS system. The hot stage was programmed for a linear rise in temperature using the Linkam TH600 heating–cooling stage.

Dynamic rheological analyses were performed using a rheometer (MCR-501, Anton-Paar). Parallel plate geometry (25-mm diameter) was used in the oscillatory mode at a constant frequency of 1 Hz while maintaining a strain of 10%. All the measurements were conducted in the atmosphere. The viscosity of the epoxy/PS system during curing was also recorded using the rheometer.

Results and Discussion

Phase separation in epoxy / polystyrene system

Curing of glycidyl phenyl ether with either 3- or 4-methyl-hexahydrophthalic anhydride as the curing agent produces a linear epoxy polymer (Figure 4.1). The polymerization is initiated by a very rapid reaction involving the opening of the anhydride ring, which results in the formation of an anion. The polymerization then propagates via the attack of the anion on the epoxy group to generate an ester-alkoxide anion, which subsequently forms an ester linkage, and a second carboxyl anion through the reaction with the anhydride. The reaction between the anion and the epoxide is considered to be the rate-determining step. Accordingly, in the curing of an acid anhydride and an epoxy monomer, the molecular weight of the product polymer does not increase significantly, and the number of polymer molecules increases with reaction conversion, such as in the radical polymerization of MMA in the presence of poly(ethylene-*co*-vinyl acetate) [7]. Thus, the phase separation process induced by curing of an acid anhydride and an epoxy is described using a ternary phase diagram, which is schematically illustrated in Figure 4.2. As the curing reaction proceeds, the composition of the mixture changes along a straight line parallel to the side connecting the vertices of the monomer A and its product polymer A. Phase separation is caused by the segregation between two different polymer species A and B, and thus the phase boundary has the shape shown in Figure 4.2.

Figure 4.3 shows an optical micrograph of the epoxy/PS = 95/5 blend after curing for 180 s at 70 °C. The uniform interdomain spacing and uniform domain size with an average periodic distance (Λ_{max}) of 2.5 μm can be clearly observed in the figure. This regular, phase-separated structure is quite similar to that obtained following isothermal SD. The SD occurs in the unstable region of the free energy curve for mixing (f) vs. concentration (c), in which $\partial^2 f/\partial c^2$ is negative. The kinetics for the early stage of SD was given by Cahn; he further simulated the phase-separated morphology as the superposition of sine waves of fixed wavelength, but with random orientations, phases, and amplitudes [16]. The characteristic features of the simulated phase-separated morphology are recognized as the co-continuity of both phase-separated phases and the uniform interdomain spacing. Therefore, the phase-separated morphology due to SD has some regularity, for example, dispersed domains with uniform sizes, even after the early stage of phase separation. Another hallmark of SD is the ring pattern observed because of light scattering, and the pattern for the present blend shown in Figure 4.4 is indicative of SD. These results, therefore, suggest that during the curing of the epoxy/PS = 95/5 blend, phase separation occurred because of SD.

Next, to study the structure development during phase separation, light-scattering studies were performed on the epoxy/PS blend during curing of the epoxy/PS = 95/5 blend. Figure 4.5 shows the evolution of the light-scattering patterns for the epoxy/PS = 95/5 blend during curing at 70 °C. Typically, no appreciable light scattering was detected for the homogeneous blend during the early stage of the reaction. After 100 s, a maximum in the scattering pattern was observed at the scattering vector $q_{max} = 2.2\ \mu\text{m}^{-1}$ ($\Lambda_{max} = 2.9\ \mu\text{m}$), indicating the development of a well-correlated, phase-separated structure. Upon further curing, q_{max} shifted to a higher value ($q_{max} = 2.5\ \mu\text{m}^{-1}$; $\Lambda_{max} = 2.5\ \mu\text{m}$) with increasing maximum intensity (I_{max}), which implied a decrease in the phase-separated structure (Λ_{max}) (arrow in Figure 4.5). These changes in the scattering profile are quite different from those observed for typical phase separation due to SD, for which q_{max} shifts to lower values with increasing maximum intensity (I_{max}) in the intermediate stage.

Furthermore, rheological measurements were obtained. Figure 4.6 shows the evolution of the complex viscosity of the epoxy/PS = 95/5 blend during curing at 70 °C. A slight increase in the observation time required for phase separation during curing at 70 °C is evident from this figure.

To verify this strange phase separation behavior quantitatively, a reduced plot of the typical parameters that characterize the early stage of SD was generated [17]. This stage can be described using Cahn's linearized theory within a good approximation, and the increase in the scattering intensity is associated with the gradient of concentration fluctuation. The linearized theory predicts that the scattered intensity in the initial period should increase exponentially with time:

$$I(q,t) \propto \exp[2R(q)t], \tag{4.3}$$

and

$$R(q) = -Mq^2\left(\frac{\partial^2 f}{\partial c^2} + 2\kappa q^2\right), \tag{4.4}$$

where $R(q)$ is the amplification factor, f is the local free energy density of mixing, M is the mobility, c is the volume fraction, κ is the concentration gradient energy density, and t is the phase separation time.

The change in the scattering intensity with time at various values of q is plotted on a semilogarithmic scale ($\ln I$ vs. q) in Figure 4.7. During the initial stage of the demixing process, the intensity varied exponentially with time at a rate that depended on q. However, deviations were observed at later times (t > ca. 110 s). The value for $R(q)$ was obtained from the slope of the linear part of the plot (early-stage SD) in Figure 4.7 using Equation (4.3).

Figure 4.8 shows a plot of $R(q)/q^2$ vs. q^2. As expected from Equation (4.4), this plot yields a good straight line for the large q regime, indicating again that the initial stage can be described within the framework of the linearized theory. From this plot, the apparent mutual diffusion coefficient D_{app}, which is defined as

$$D_{app} = -M\left(\frac{\partial^2 f^{\,2}}{\partial c^2}\right) \tag{4.5}$$

was estimated. According to Equation (4.5), D_{app} is obtained from the intercept on the vertical axis in Figure 4.8. Note that the above analysis is based on the assumption that M, κ, and $f(c)$ are constant (independent of time). In general, this assumption is not satisfied in reactive systems. However, the linear relationships in Figures 4.7 and 4.8 may suggest that the assumptions are approximately true in the very early stage of this phase separation with reaction (curing time < 110 s). Such behavior has also been reported in other reactive systems, such as curing-induced phase separation [2] and polymerization-induced phase separation [7].

The parameters $q_m(0)^2$ and D_{app} for the scaling analyses with the reduced parameters $Q_m(0)$ and τ were then required. The characteristic time t_c was defined as follows:

$$t_c = [q_m{}^2(0)D_{app}]^{-1}, \tag{4.6}$$

and τ was defined as follows:

$$\tau = t/t_c. \tag{4.7}$$

Here, for the sake of simplicity, t = 100 was set as the starting time for phase separation based on the results shown in Figures 4.5 and 4.7.

The reduced wavenumber $Q_m(t)$ was then defined for the dominant Fourier component of the fluctuations as follows:

$$Q_m(\tau) = q_m(\tau)/q_m(0). \tag{4.8}$$

Figure 4.9 shows the plot of the reduced variable $Q_m(\tau)$ for the epoxy/PS blend during curing as a function of increasing quench depth. The reduced wavenumber for the dominant mode of the fluctuations $Q_m(\tau)$ was determined using Equations (4.6)~(4.8). The quantities $q_m(0)$ and D_{app} were obtained from the experimental data for the early stage of SD. Figure 4.9 also shows the change in $Q_m(\tau)$ on the basis of previously reported data for the isoquench depth analysis of a poly(vinyl methyl ether)/PS blend [17]. As shown in the figure, the phase separation process for the epoxy/PS blend was different from the conventional isoquench depth process in the following respects: (i) there is significantly more time before any observable fluctuation and (ii) the periodic distance of the resulting two-phase structure in the later stages decreases. These phenomena related to the time evolution of phase separation were predicted by the initial computer simulation using the Cahn–Hilliard nonlinear diffusion equation [6], *i.e.*, (i) the initial concentration profile was preserved, even at the deepest quench depth for when the quench depth increased rapidly, and (ii) a rapidly growing concentration fluctuation with a shorter periodic distance appeared and overlapped with the previous one when the quench depth increased slowly.

Phase separation in epoxy / epoxy system

To further investigate the influence of a continually increasing quench depth on phase separation, an epoxy/epoxy system (monomer A/monomer B) with the simple phase diagram for a symmetrical mixture was selected for comparison with the epoxy/PS system described above.

In this case, USAXS analysis of an epoxy (diglycidyl aminophenol)/epoxy (diglycidyl ether of bisphenol A) = 50/50 blend was performed during curing to study the structure development through phase separation because this system has a very small periodic phase separation distance on the order of several hundred nanometers. Figure 4.10 presents typical experimental data for the time evolution of the scattering intensity for the epoxy/epoxy = 50/50 blend during curing at 180 °C. The scattering maximum first developed at a scattering vector (q_{max}) of approximately 0.00937 nm^{-1} (Λ_{max} = 670 nm) and appeared to be stationary for a short time, indicating the early SD stage. It then rapidly moved to higher scattering vector (q_{max} = 0.0101 nm^{-1}; Λ_{max} = 620 nm) in the intermediate SD stage, thus behaving similar to the epoxy/PS system. A reduced plot of the key parameters characterizing the early SD stage was also prepared (Figure 4.11) in the same manner as presented for the epoxy/PS system.

In Figure 4.11, the plot of the reduced variable $Q_m(\tau)$ for the epoxy/epoxy blend during phase separation is shown along with that for the epoxy/PS blend. As shown in the figure, changes in $Q_\mathrm{m}(\tau)$ were similar for the two systems. During the initial stage of the demixing process, $Q_m(\tau)$ remained constant, but as curing proceeded, $Q_\mathrm{m}(\tau)$ shifted to higher values, implying a decrease in the size of the phase-separated structure.

Conclusion

The effects of phase separation on the time evolution of the polymerization process were studied. The kinetics of SD for a binary epoxy/PS blend during polymerization was thoroughly investigated using a time-resolved light-scattering technique. The early stage of SD for this system was well described within the framework of the Cahn–Hilliard linearized theory. On the other hand, during the later stage of SD for this system, the phase separation during the polymerization process was quite different from the phase separation observed for isoquench depth conditions in two respects: (i) for non-isoquench conditions, it takes more time before an observable fluctuation appears, and (ii) the periodic distance of the resulting two-phase structure in the later stages decreases with time. Similar phenomena were also observed for the time evolution of the phase separation during the polymerization of an epoxy/epoxy blend.

Chapter 5.

Structure Development by Reaction-Induced Phase Separation in Polymer Mixtures: Computer Simulation under the Non-isoquench Depth

Introduction

The computer simulation for the growth of a concentration fluctuation is given on the basis of Cahn-Hilliard non-linear diffusion equation [1]. In this simulation, first, a homogeneous system is allowed to demix isothermally for a while at a shallow quench, and then the mixed system undergoes a successive increasing quench depth at a constant rate. For the case of a fast increasing quench depth rate (6°C/s), the initial concentration profile is preserved, and then the profile becomes rectangular, The periodic distance and amplitude of the initial fluctuation are maintained even at the deepest quench depth. On the other hand, for the case of a slower increasing quench depth rate (3°C/s), initial concentration profile becomes rather rectangular with successive increasing quench depth but the periodic distance remains constant. Then a rapid glowing concentration fluctuation with a shorter periodic distance appears and overlaps with a previous one.

Also, there have been several theoretical attempts to investigate the phase separation processes under chemical reactions by using the time-dependent Ginzburg−Landau (TDGL) model with chemical reaction terms in low-molecular-weight materials [2-3]. And there have been very few trials to extend the TDGL model to complex polymeric systems under polymerization. Few examples of such trials were made using the dynamic self-consistent field (SCF) theory [4-5]. Using such dynamical SCF theory, one can take the molecular architecture and the conformation of the constituent polymer chains into account through the path integral calculation.

In this chapter, in order to verify the influence of the successive increase of quench depth to phase separation, we carried out computer simulation by using multi-scale modeling in the field of polymeric materials the OCTA [6] on the phase separation in these systems under the successive increase in the thermodynamic quench.

Theory

Dynamical mean field theory for chemical reaction

Computer simulations based on the mean-field approximation are useful for studying the phase separation of polymeric systems. The SCF method is one such example. Combined with path-integral formalism, the SCF method can be used to evaluate the conformational entropy of polymer chains, considering the various chain architectures. Theoretical calculations based on the SCF theory were thus performed using the “Simulation Utilities for Soft and Hard Interfaces (SUSHI)” program in the OCTA system, which is publicly available on the Web [6]. An extension of this SCF technique to dynamic phenomena, such as the phase separation of polymer blends, has been proposed [7]. Furthermore, it is possible to incorporate chemical reactions into the dynamic SCF method, which enables the study of phase separation processes induced by chemical reactions.

The time evolution of the concentration of species K (K = polymer A or B or monomer a or b), $\phi_K(r, t)$, obeys the following diffusion equation with the transport coefficient L_K:

$$\frac{\partial \phi_K(r,t)}{\partial t} = \nabla L_K \nabla \frac{\delta F}{\delta \phi_K(r,t)}, \qquad (5.1)$$

where F is the free energy of the system determined using the path-integral method. The free energy F can be described as follows [8]:

$$F(\phi_i) = \sum_i \int dr \frac{1}{N_i} \phi_i \ln \phi_i + \sum_{i,j} \int dr \chi \phi_i \phi_j + \sum_{i,j} \int dr \frac{1}{36 \phi_i \phi_j} \left(\left| \nabla \phi_i \right|^2 + \left| \nabla \phi_j \right|^2 \right), \qquad (5.2)$$

where N_i and N_j are the lengths of the i-th chain of polymer A and the j-th chain of polymer B respectively, and χ is the interaction parameter between polymer A and polymer B. This free energy model is called the Flory–Huggins–de Gennes model, and it can be used for the simulation of polymer blends.

By adding a reaction term to the right-hand side of Equation (5.1), the time evolution of the segment density during a chemical reaction can be described. When the characteristic time scale of the reaction is considerably faster than the diffusion rates for the polymers, such as in epoxy polymerization reactions, it is reasonable to assume that the monomers are instantaneously converted to the polymer with a certain degree of polymerization. To focus on the coupling between the phase separation and the polymerization, we therefore drastically simplified the model as described in the following equations:

$$\frac{\partial \phi_K(r,t)}{\partial t} = \nabla L_K \nabla \frac{\delta F}{\delta \phi_K(r,t)} + \left.\frac{\partial \phi_K(r,t)}{\partial t}\right|_{react}, \qquad (5.3)$$

$$\left.\frac{\partial \phi_A(r,t)}{\partial t}\right|_{react} = k\phi_{end}(r,t)\phi_a(r,t), \qquad (5.4)$$

$$\left.\frac{\partial \phi_B(r,t)}{\partial t}\right|_{react} = k\phi_{end}(r,t)\phi_b(r,t), \qquad (5.5)$$

$$\left.\frac{\partial \phi_a(r,t)}{\partial t}\right|_{react} = -k\phi_{end}(r,t)\phi_a(r,t), \qquad (5.6)$$

$$\left.\frac{\partial \phi_b(r,t)}{\partial t}\right|_{react} = -k\phi_{end}(r,t)\phi_b(r,t). \qquad (5.7)$$

We can assume the unit to be unity by choosing appropriate units for the time t_0 and length l_0. Here, for simplicity, it was assumed that the kinetic constants L_A and L_B are equal. This special condition is justified when the sizes of the segments A and B are equal because L_A and L_B are the kinetic coefficients for the segments, respectively. It should also be noted that the right-hand sides of Equations (5.4)～(5.7) are reaction terms, where k is a model reaction constant for the polymerization reaction.

Experimental

The dynamic SCF simulation was performed using the SUSHI program in the OCTA system [6]. The SCF simulations were performed on a machine with dual Xeon CPUs (Quad Core 2.4 GHz) and dual GPUs (NVIDIA Tesla C2075). The simulations were performed on a rather small system with 34 × 34 meshes divided by two (total 64 × 64 meshes) with up to 35000 steps and $\Delta t = 5 \times 10^{-5}$. A periodic boundary condition was imposed on each side.

The initial time step width Δt for the simulation was established, and then the time step ratio r_t (> 1) and upper limit for the time step width Δt_{max}, which was treated as a variable, were introduced. The time step width Δt was then modified according to the following algorithm:

(1) Set the initial Δt.

(2) Perform a one-step calculation of the dynamics simulation.

(3) If some of the segment densities are negative, return to the state just prior to step (2). Change Δt as $\Delta t \leftarrow \Delta t / r_t$ and then recalculate step (2). Otherwise, go to step (4).

(4) Change Δt as $\Delta t \leftarrow \Delta t / r_t$. If Δt exceeds Δt_{max}, then $\Delta t \leftarrow \Delta t_{max}$.

(5) Increase the time of the simulation system by Δt and go to step (2).

This acceleration technique is effective for determining the structural changes in a system in the early and very late stages after the system nearly reaches its equilibrium structure. Large values for Δt are automatically chosen for such early and very late stages.

Results and Discussion

Figure 5.1 shows the phase diagram of a symmetrical polymer mixture [9]. The critical point is located at $\phi = 0.5$, $\chi N = 2$. The binodal curve is given by the following equation:

$$\chi_b N = \frac{1}{2\phi - 1} \ln \frac{\phi}{1 - \phi}, \tag{5.8}$$

and the spinodal curve is given by

$$\chi_s N = \frac{1}{2\phi(1 - \phi)}, \tag{5.9}$$

where χ_b and χ_s are the χ parameters for the binodal and spinodal curves, respectively. A series of dynamic simulations on a 2D system, starting from a uniform mixture of epoxy monomers, was performed by changing the value of the reaction constant k. Here, for simplicity, the value of ϕ was assumed to be 0.5. The system was a 2D system composed of 64 × 64 square meshes with a mesh width of $\Delta x = 0.1$. The TDGL equations (Equations (5.3)~(5.7)) were numerically integrated using the Euler scheme with a time mesh $\Delta t = 5.0 \times 10^{-5}$. The initial sizes of the epoxy monomers were both set at $N = 1$, and the epoxy polymer sizes were set at $N = 5$. Throughout this study, the χ parameter was selected to fall between each epoxy segment at 1.0 and is denoted as χ. Therefore, the initial value for χN (N is the total chain length of the epoxy monomer) is 1.0 × 1 = 1.0 (point I in Figure 5.1), while the end value for χN is 1.0 × 5 = 5.0 (point III in Figure 5.1).

First, the phase separation morphology due to SD with an isoquench depth (point III in Figure 5.1) was examined. In Figure 5.2, the time evolution (0–30000 *steps*) of the phase separation morphology with $\chi N = 5$ (const.) is illustrated. In this case, it can be seen that at an early stage of demixing (up to 10000 *steps*), a fluctuation appeared and grew while its periodic distance remained constant. A coarsening of the phase-separated structure then occurred at a later stage of demixing. These calculation results thus describe the demixing behavior for conventional SD, *i.e.*, growth of a fluctuation with a fixed periodic distance in the early stage of SD followed by structure coarsening via an evaporation/condensation mechanism with an increase in the periodic distance with time in the later stage of SD.

Figure 5.3 shows the Fourier transform spectra for the evolution of the phase separation morphology presented in Figure 5.2. In this figure, it can be clearly seen that the average periodic distance (Λ_{max}) remained nearly constant during the early stage of demixing (5000–10000 *steps*) and then increased during the later stage of demixing (> 10000 *steps*).

The phase separation morphology during SD with a continually increasing quench depth was then investigated. In these simulations, the value of χN changes from 1 to 5 (arrow in Figure 5.1). Figure 5.4 presents the temporal evolution (0–35000 *steps*) for the phase separation morphology with a continually increasing quench depth (χN: 2 to 5). The Fourier transform spectra for the time evolution of the phase separation morphology shown in Figure 5.5 are presented in Figure 5.4.

Here, the reduced wavenumber $Q_m(t)$ for the dominant Fourier component of the fluctuations was defined as follows:

$$Q_m(step) = q_m(step) / q_m(5000)\,. \qquad (5.10)$$

Figure 5.6 shows a plot of the reduced variable $Q_m(step)$ with a continually increasing quench depth along with the results for an isoquench depth of $\chi N = 5$ (const.) for comparison. For the isoquench depth, no change in $Q_m(step)$ is observed during the early stage, and $Q_m(step)$ shifts to lower values during the later stage. On the other hand, when the quench depth increases continuously, no change in $Q_m(step)$ is observed even at < ca. 20000 *steps*, and then as the quench depth further increases, $Q_m(step)$ shifts to higher values. The simulated results presented in Figure 5.6 for a continually increasing quench depth indicate that the periodic distance for the resulting two-phase structure in the later stages decreases with time. As is clearly shown in Figure 5.5, a smaller periodic distance for the fluctuation appears at larger quench depths. Therefore, the scattering results in Figures 4.5 and 4.10 may correspond to the simulation results in Figure 5.6.

From the linearized theory in the early stage, q_m is given as follows [8]:

$$q_m \sim \left|\chi - \chi_s\right|^{1/2} \sim \left|T - T_s\right|^{1/2} . \qquad (5.11)$$

Equation (5.11) predicts that a continually increasing quench depth always leads to an increase in q_m, which implies the consistent development of a new dominant Fourier component of concentration fluctuation for larger q_m. Quantitatively, the Cahn–Hilliard approach gives the difference in the local concentrations for the initial miscible region and the current immiscible region, $\delta c(\boldsymbol{r}, t)$, as a superposition of the harmonics of the wavenumber, which are represented as the amplification factor ($R(\boldsymbol{q})$) according to

$$\delta c(\vec{r}, t) = \sum_{all\vec{q}} \exp\left[R(\vec{q})t\right]\left\{A(\vec{q})\cos(\vec{q}\cdot\vec{r}) + B(\vec{q})\sin(\vec{q}\cdot\vec{r})\right\}, \qquad (5.12)$$

$$R(\vec{q}) = -Mq^2\left(\frac{\partial^2 f}{\partial c^2} + 2\kappa q^2\right) , \qquad (5.13)$$

where f is the local free energy density of mixing, M is the mobility, c is the volume fraction, κ is the concentration gradient energy density and t is the phase separation time. The behavior of $R(\boldsymbol{q})$ as the quench depth continually increases is schematically illustrated in Figure 5.7. As shown in the figure, a continual increase in the quench depth always results in a larger value for q_m, which implies the consistent development of a new dominant Fourier component for the concentration fluctuation of larger q_m. Thus, during the early stage of phase separation, it takes more time for an observable fluctuation to appear, and during the later stage of phase separation, a new concentration fluctuation with a shorter periodic distance (larger q_m) appears.

Conclusion

Computer simulations using the dynamic SCF method were then performed to interpret the morphology formation during demixing driven by chemical reactions, for which the quench depth continually increased. The simulation results suggest that the periodic distance of the resulting two-phase structure formed in the later stages decreases with time. Furthermore, the time dependence of the concentration fluctuations observed in these simulations provided a satisfying explanation for the morphologies formed as a result of a continuously increasing quench depth.

Chapter 6.

General Conclusion

In this thesis, we have studied on structure development of polymer blends under the continuous change of quench depth, such as a spinodal decomposition (SD) induced by chemical reaction.

In chapter 2, we have found that the phase separation during polymerization of MMA in the presence of EVA can be interpreted in terms of a phase separation scheme based on SD, which is induced by the increasing of PMMA content in the mixture. This phase separation behavior is different from the ordinary isothermal SD. The final phase-separation structure may be formed by interruption of a co-continuous percolation structure to the cluster structure.

In chapter 3, we selected a binary mixture of polystyrene and poly (vinyl methyl ether) having the lower critical solution temperature (LCST) in order to verify the influence of the successive increase of quench depth to phase separation and we carried out light scattering studies in this system under the successive increase in the thermodynamic quench by the continuous increase of temperature with time. We have found that the phase separation behavior under the continuous change of quench depth is different from the ordinary isothermal quench depth in the following points: (i) For the continuous change of quench depth there is much time (reduced parameter τ defined by parameters characterizing the early stage of SD) until arising the observable fluctuation; and (ii) after growing fluctuation $Q_m(\tau)$ is slowly decreasing with τ.

In chapter 4, we selected two binary mixtures; epoxy / polystyrene system, having a linear epoxy polymer by a simple polymerization such as curing of an acid anhydride and an epoxy monomer, and epoxy / epoxy system, having a simple phase diagram of a symmetric mixture in order to verify the influence of the successive increase of quench depth to phase separation. We have found that this phase separation process under polymerization process was quite different from the phase separation process under the familiar isoquench depth in the following point: (i) For the non-isoquench it takes much time until arising the observable fluctuation; and (ii) the periodic distance of the resulting two-phase structure in the later stages gets smaller with time. And similar phenomena of the phase separation on the time evolution of the polymerization process was observed in the binary epoxy / epoxy blend.

In chapter 5, in order to verify the influence of the successive increase of quench depth to phase separation, we carried out computer simulation by using multi-scale modeling in the field of polymeric materials the OCTA on the phase separation in these systems under the successive increase in the thermodynamic quench. The simulation results suggest that the periodic distance of the resulting two-phase structure in the later stages gets smaller with time. The time dependences of concentration fluctuations observed in these simulations provide a nice explanation for the morphologies formed by the continuous change of quench depth.