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Tricontinuous structure in a homopolymer–homopolymer–random-copolymer ternary mixture quenched under the tricritical point

Mikihito Takenaka and Takeji Hashimoto*
Division of Polymer Chemistry, Graduate School of Engineering, Kyoto University, Kyoto 606-01, Japan

Toshiaki Dobashi
Department of Biological and Chemical Engineering, Faculty of Engineering, Gunma University, Kiryu 516, Japan

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We proposed a dynamical method to simulate the time change in the domain structure for a homopolymer–homopolymer–random-copolymer ternary mixture quenched under its tricritical point. The system studied underwent a phase separation into tricontinuous domain structure. The growth of the domain structure obeys a $t^{-1/3}$ power law and the dynamical scaling law is valid in the late stage of phase separation.

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It is well known that the phase transition processes of binary mixtures quenched into their unstable region progress via spinodal decomposition (SD). The dynamics of the SD processes of binary mixtures have been investigated theoretically and experimentally in the field of small molecules, metallic alloys, and inorganic glasses [1,2]. Many authors reported experimental [3,4], theoretical [5–8], and computational [9–11] studies of the dynamics of the SD processes of binary polymer blends as well as other binary mixtures. Most investigations of polymer blends focused on the universality in the dynamics of SD processes in polymer blends, such as the validity of the scaling postulate [12] and the dynamical scaling law [13]. Recently, Leibler [14] and Broseta and Fredrickson [15] investigated the phase diagrams of a ternary mixture of polymer A, polymer B and a random copolymer composed of A and B comonomers. One component of the investigations of the phase diagram of the homopolymer–homopolymer–random-copolymer ternary mixture is that the ternary mixture has a tricritical point and separates into three phases under the tricritical point [15].

The aim of the present paper is to propose a method for the phase separation processes of the ternary mixtures quenched under the tricritical point, and to show the computational results with the dynamical model.

Leibler and Broseta and Fredrickson approximated the free-energy density per monomer by the Flory-Huggins lattice theory to investigate the phase diagram of the ternary mixture. Here we employ the Flory–Huggins–de Gennes (FHD) theory [5] to simulate the phase separation process of the ternary mixtures, where the nonlocal term is added to the Flory-Huggins theory.

We consider the system A-B-R where A and B denote different homopolymer species, and R denotes a random copolymer consisting of equal volume fractions of A and B monomers. If the volume fraction of A, B, and R, at a point $\mathbf{r}$ and a time t are defined by $\phi_A(\mathbf{r},t)$, $\phi_B(\mathbf{r},t)$, and $\phi_R(\mathbf{r},t)$, respectively, the incompressibility condition can be expressed by

$$\phi_A(\mathbf{r},t)+\phi_B(\mathbf{r},t)+\phi_R(\mathbf{r},t)=1 , \tag{1}$$

and only two of the three volume fractions can be recognized as independent parameters in the system. Here $\phi_A(\mathbf{r},t)$ and $\phi_B(\mathbf{r},t)$ are selected as independent parameters. From continuity equations and Onsager theory for A and B, we obtain the following basic equation to describe the time evolution of $\phi_A(\mathbf{r},t)$ and $\phi_B(\mathbf{r},t)$:

$$\frac{\partial\phi_A(\mathbf{r},t)}{\partial t}=\Lambda_{AA}\nabla^2(\mu_A-\mu_R)+\Lambda_{AB}\nabla^2(\mu_B-\mu_R) \tag{2}$$

and

$$\frac{\partial\phi_B(\mathbf{r},t)}{\partial t}=\Lambda_{BA}\nabla^2(\mu_A-\mu_R)+\Lambda_{BB}\nabla^2(\mu_B-\mu_R) , \tag{3}$$

where Λ_{kk} and μ_k ($k=A$ or B) are the Onsager coefficient and the chemical potential of the k polymer, respectively. In Eqs. (2) and (3), we neglect the thermal noise [16] and the hydrodynamic interaction [17–19].

The chemical potential of k can be obtained from the total free-energy functional $F\{\phi_A,\phi_B,\phi_R\}$ for the system. $F\{\phi_A,\phi_B,\phi_R\}$ is given by [20]

$$\begin{aligned}F\{\phi_A,\phi_B,\phi_R\}/k_BT &=\frac{\phi_A}{N_A}\ln\phi_A+\frac{\phi_B}{N_B}\ln\phi_B+\frac{\phi_R}{N_R}\ln\phi_R\\ &\quad+\chi\phi_A\phi_B+\tfrac{1}{4}\chi(\phi_A+\phi_B)\phi_R\\ &\quad+\sum_{k=A,B,R}\frac{a^2}{36\phi_k}(\nabla\phi_k)^2\end{aligned} \tag{4}$$

where k_B is the Boltzmann constant, T is the absolute temperature, χ the Flory-Huggins interaction parameter for the pair of A and B monomers; a the statistical segment length, and N_k the polymerization index of k. Here we assume that the statistical segment length of monomer A is identical to that of monomer B. The standard definition of μ_k gives

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*Author to whom correspondence should be addressed.

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$$\mu_k = F + \sum_{j=A,B,R} \frac{\delta F}{\delta \phi_j}(\delta_{kj} - \phi_j) , \tag{5}$$

where δ_{kj} is the Kronecker delta.

Under the incompressibility condition, the Onsager coefficients of the system are expressed by [11]

$$\Lambda_{AA}^{-1} = \Lambda_{A0}^{-1} + (\Lambda_{B0} + \Lambda_{R0})^{-1} , \tag{6}$$

$$\Lambda_{BB}^{-1} = \Lambda_{B0}^{-1} + (\Lambda_{A0} + \Lambda_{R0})^{-1} , \tag{7}$$

and

$$\Lambda_{AB}^{-1} = \Lambda_{BA}^{-1} = -\left[\Lambda_{A0}^{-1} + \Lambda_{B0}^{-1} + \frac{\Lambda_{R0}}{\Lambda_{A0}\Lambda_{B0}} \right] , \tag{8}$$

where Λ_{k0} is the bare mobility of k given by [5]

$$\Lambda_{k0} = D_k N_k \phi_k , \tag{9}$$

with D_k being the self-diffusion coefficient of k.

We have numerically integrated Eqs. (2) and (3) on a 128×128 lattice with a time step of 0.000 05 s and a lattice width of 1.0 nm. The periodic boundary conditions are imposed on each box side. In order to reduce the computation time, we replaced $1/\phi_k$ in Eq. (4) and ϕ_k in Eq. (9) by $1/\langle \phi_k \rangle$ and $\langle \phi_k \rangle$, respectively, where $\langle \phi_k \rangle$ is the space average ϕ_k at $t=0$. The initial configurations of the fields of ϕ_A and ϕ_B are given according to Gaussian random numbers with $\langle \phi_A \rangle = \langle \phi_B \rangle = 0.17$. The parameters chosen here are $N_A = N_B = 1000$, $N_R = 500$, $a = 0.7$ nm, $D_A = D_B = 2000$ nm^2/s, and $D_R = 8000$ nm^2/s. According to Broseta and Fredrickson, the system with the parameters listed above has the tricritical point at $\chi = 0.01$, so that we used $\chi = 0.0104$. We have run five independent computations with different initial configurations up to 2500 s and averaged the results. To investigate the growth of the domain structures quantitatively, we calculate the circularly averaged scattering structure factor $I_k(q,t)$ of the field ϕ_k (hereafter designated the "partial structure factor") as a function of time t, where $I_k(q,t)$ is defined by

$$I_k(q,t) = \frac{1}{2\pi} \int_0^{2\pi} I_k(q,t) d\mu , \tag{10}$$

where μ is the azimuthal angle of wave vector $\mathbf{q}$ with respect to the x axis, and q is the magnitude of the wave vector.

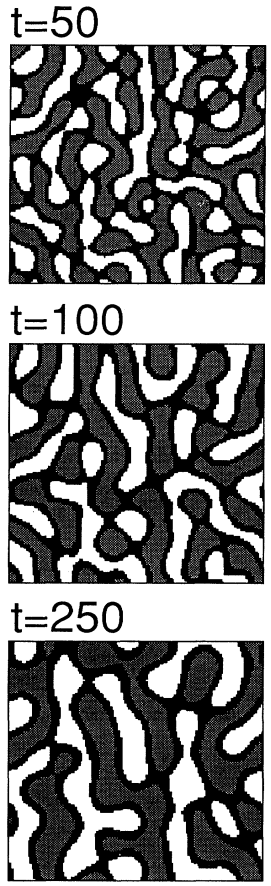

FIG. 1. Snapshot pictures at $t = 50$, 100, and 250 s. Black, gray, and white parts correspond to $\delta\phi_R > \delta\phi_A$ and $\delta\phi_R > \delta\phi_B$, $\delta\phi_A > \delta\phi_R$ and $\delta\phi_A > \delta\phi_B$, and $\delta\phi_B > \delta\phi_A$ and $\delta\phi_B > \delta\phi_R$ regions, respectively, where $\delta\phi_R = \phi_R - \langle \phi_R \rangle + 0.04$, $\delta\phi_A = \phi_A - \langle \phi_A \rangle$, and $\delta\phi_B = \phi_B - \langle \phi_B \rangle$. Each picture has 128×128 meshes, with a lattice size of 1 nm.

Figure 1 shows domain structures corresponding to the fields of ϕ_A, ϕ_B, and ϕ_R. The ϕ_A-, ϕ_B-, and ϕ_R-rich regions form continuous structures ("tricontinuous structures"), and grow with time. The patterns of ϕ_A and ϕ_B seem to grow with self-similarity, which is similar to those of binary mixtures. The distribution of ϕ_R shows that the random copolymer tends to accumulate at interfaces between A- and B-rich regions. This accumulation is similar to the accumulation of a surfactant in binary mixtures [21]. However, there is a fundamental difference between the two systems: the A-r-B-rich region grows with time because we performed the simulation under the tricritical point, whereas the surfactant-rich region in binary mixtures does not grow with time [21].

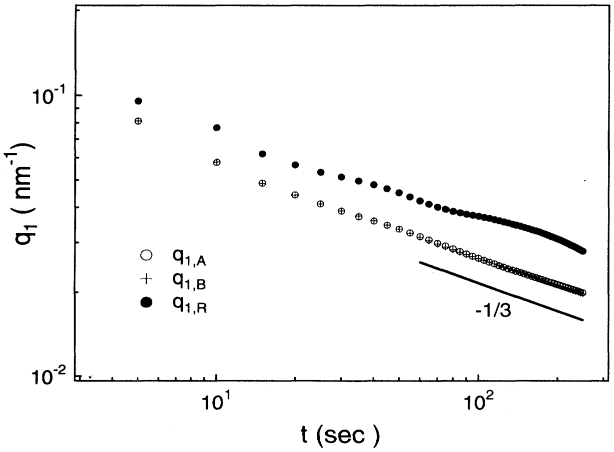

FIG. 2. Time changes in the characteristic wave numbers q_{A1}, q_{B1}, and q_{R1} in a double logarithmic scale.

In Fig. 2, the first moments $q_{1k}(t)$ of $I_k(q,t)$ are plotted as a function of t, where $q_{1k}(t)$ is defined by

$$q_{1k}(t)=\frac{\int qI_k(q,t)dq}{\int I_k(q,t)dq} . \tag{11}$$

Time changes in $q_{1A}(t)$ and $q_{1B}(t)$ are superimposed completely because of the symmetry features, such that the polymerization indices and initial volume fractions of A and B are identical. The decreases of $q_{1A}(t)$ and $q_{1B}(t)$ obey the power law $t^{-1/3}$ at the long time limit covered in our computation, identical with the results of computer simulations for the binary mixture without hydrodynamic interactions [22]. Although the absolute value of $q_{1R}(t)$ is different from those of $q_{1A}(t)$ and $q_{1B}(t)$, $q_{1R}(t)$ is approximately given by the same power law $t^{-1/3}$ at the long time limit. This indicates that A-r-B-rich phase grows with time as well as the other two phases. These time changes are very different from that in the characteristic wave number $q_m(t)$ of the A-B-surfactant, where $q_m(t)$ of the A-B-surfactant system corresponds to $q_{1A}(t)$ or $q_{1B}(t)$ in the A–B–A-r-B system. For the A-B-surfactant system, the accumulated surfactant reduces the interfacial tension between A- and B-rich phases so that the growth rate of the domains structures deviates from $t^{-1/3}$ [21].

We investigated whether the dynamical scaling law is valid or not for the time change in the three-phase separated domain structure of the ternary system, by calculating the scaled partial structure factor $S_k(q,t)$ of the k component defined by

$$S_k(x,t)=q_{1k}^2(t)I_k(q,t) , \tag{12}$$

with the reduced wave number

$$x=q/q_{1k}(t) . \tag{13}$$

The scaled partial structure factors of each component are plotted as function of x in the late stage in Fig. 3. $S_A(x,t)$ and $S_B(x,t)$ are well superimposed and independent of time, indicating that the dynamical scaling law is valid for the time changes in the A and B-rich domain structures. It is noted that a shoulder at $x=2$, due to the domain being locally packed alternating lamellae [10,23], can be observed in $S_A(x,t)$ and $S_B(x,t)$, as in the scaled structure factor in symmetric binary mixtures [10,23]. However, the position of the shoulder for symmetric binary mixtures is reported to be at $x=3$ [10,23]. This difference arises from the difference in the volume fractions of the A- or B-rich domain in the ternary and binary mixtures: In the case of the symmetric binary mixture, the volume fractions of two coexisting domains become identical, which causes the shoulder at $x=2$ to disappear. This disappearance is simply because the form factor from the single lamellae reaches a minimum at $x=2$. On the other hand, in the case of the ternary mixture, such a disappearance does not occur. For the (A-B)–A–B (the system composed of A-B blockcopolymer, homopolymer A, and homopolymer B) system, the shoulder at $x=3$ is more enhanced than that of the A–B system, because the blockcopolymer A-B enlarges the persistent length of the local lamellae structure in the system [21]. The asymptotic behavior of $S_A(x,t)$ and $S_B(x,t)$ at $x<1$ obeys x^4, which agrees with the experimental [23], theoretical [24,25], and computational [19] results for symmetric binary mixtures. The power law exponent m in the scaled partial structure factors of $S_k(x,t) \sim x^{-m}$ ($k=A$, B, and R) at $x>1$ is much larger than that of 3 expected for the Porod law in two dimensional space, because the interface thickness is still thick [22].

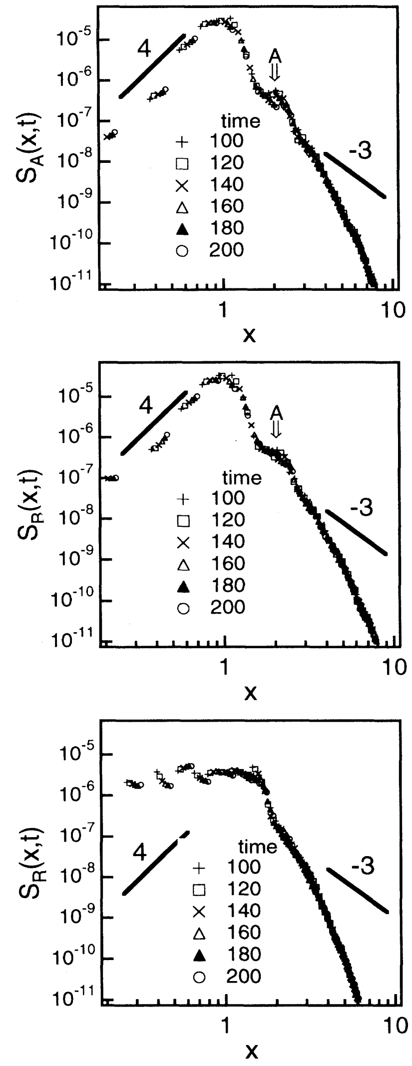

FIG. 3. Scaled structure factors plotted as a function of the reduced wave number x for A, B, and R in the time region from $t=100$–200 s.

$S_R(x,t)$ obtained at various times in the late stage are also superimposed, and the time change in the random copolymer domains retains the dynamical scaling law. $S_R(x,t)$ is much broader than $S_A(x,t)$ and $S_B(x,t)$, and the shoulder at $x=2$ in $S_R(x,t)$ is less distinct. The slope of $S_R(x,t)$ at $x<1$ is much smaller than 4. These two effects may be interpreted as arising from a large distribution of the domain spacing of the random copolymer phase, compared with those of the A- and B-rich regions shown in Fig. 1. Similarly to $S_A(x,t)$ and $S_B(x,t)$ the slope m of $S_R(x,t)$ at the high-x region is larger than 3, because of the effects of the interface thickness.

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