

PHASE SEPARATION OF POLYMER SOLUTIONS IN THE METASTABLE REGION

Kenji Kubota

Department of Biological and Chemical Engineering, Faculty of Technology,
Gunma University, Kiryu, Gunma 376, Japan

INTRODUCTION: It has become an important subject to study the molecular mechanism of phase separation of the polymer solution in its unstable region. In the metastable region, the phase separation will proceed by nucleation and growth. In general, the dominant mechanism which limits the dynamical behavior in the process of phase separation is described by a system-independent diffusion process. Recently, Bates et al. studied the phase separation (nucleation-growth) in the metastable region using an oligomer blend, and observed the growth of droplets consisted of minority phase as $R(t) \sim t^{1/2}$ in accordance with the diffusion limited growth mechanism [1]. However, the polymer system has characteristic time and length scales intrinsic to the polymer structure, and the dynamic process controlled by these scales can become the elementary molecular dynamics. Especially, the entanglements between the polymer chains and the asymmetry in the molecular size and mobility between the polymer and the solvent molecules should play an important role in the phase separation. Moreover, the existence of intermediate stage between the growth and coarsening stage was predicted theoretically by Tokuyama recently [2]. Here, the light scattering study of the time evolution of phase separation and the growing mechanism of minority phase in a supercooled polymer solution is investigated from the growth to the coarsening stage.

EXPERIMENTAL: We studied the growth mechanism of minority (concentrated) phase in the metastable region of very dilute polymer solution. The quenched condition is far apart from the critical point. The phase diagram is shown in Fig. 1. We have employed two solutions of polystyrene (PS) having molecular weight (M_w) of 60×10^4 in diethyloxalate (DEO) and PS having $M_w = 650 \times 10^4$ in diethylmalonate (DEM). PS are the well fractionated and monodispersed samples. The molecular weights of them are high enough to make sufficient entanglements. DEO and DEM are the solvents having almost the same density as that of PS. Therefore, the observation of the phase-separating process over a very long time period (growth to coarsening stage) was possible without sedimentation and precipitation. The characteristic molecular parameters of the present study were tabulated in Table 1. The critical

concentration and temperature are 46.6 mg/g and 39.630°C for PS/DEO and about 20 mg/g and 34°C for PS/DEM. Very dilute solutions with concentrations of 0.40 mg/g (PS/DEO) and 0.21 mg/g (PS/DEM) (both are about 1/100 of the critical concentration) were used in the present study in order to avoid multiple-scattering effect. The quench depth ΔT was in the order of 0.1°C or less. We used the dynamic light scattering technique to determine the mean radius $R(t)$ and the number density $N(t)$ of growing droplets as a function of the elapsed time t . When two species of different sizes exist in the scattering medium, the intensity correlation function $G^2(t)$ has a double-exponential form (see Fig.) as

$$G^2(t) = \langle I(\theta) \rangle^2 [1 + \beta |g^1(t)|^2] \quad (1)$$

$$\text{and} \quad g^1(t) = A_1 \exp(-D_1 q^2 t) + A_2 \exp(-D_2 q^2 t) \quad (2)$$

where $\langle I(\theta) \rangle$ is the scattered intensity at the scattering angle of θ , β is the machine constant, and $g^1(t)$ is the normalized field-correlation function. A_1 and A_2 are the scattered intensity of smaller and larger particles, respectively. D is the diffusion coefficient and is related to the radius for the spherical particles by the well-known Stokes-Einstein equation $D = k_B T / 6\pi\eta R$ with η being the solvent viscosity. q is the scattering (momentum transfer) vector. For the present phase-separating polymer solution in the metastable region, the smaller particle is the individual polymer chain molecule and the larger one is the growing droplet of the minority phase. In fact, the hydrodynamic radius of the smaller particle coincides essentially with that of the individual polymer chain. Zero-angle scattered intensity $I_{2,0}$ of the growing droplets was evaluated from A_2 by use of the scattering function of sphere introducing the size distribution assuming the Gaussian distribution, and $I_{2,0}$ is proportional to NR^6 . In reality, the scattered light intensity profile as a function of scattering angle was well reproduced by the variance of 0.1 indicating a fairly narrow distribution and by the radius determined by the double-exponential fit to the correlation functions.

Table 1. Characteristic values of samples

	molecular weight	density (at 20°C)	refractive index
polystyrene	600,000 (Mw/Mn < 1.10)	1.075	1.591
diethyloxalate	146	1.079	1.4104
polystyrene	6,500,000 (Mw/Mn < 1.06)	1.075	1.591
diethylmalonate	160	1.049	1.414

RESULTS AND DISCUSSION: Figures 3 to 6 show the double-logarithmic plots of the time evolution of the droplet size $R(t)$ and the zero-angle scattering intensity $I_{2,0}$ as a function of the elapsed time after the quench into the metastable region for PS/DEO and PS/DEM. From these experimental

results, the following features about the time evolution of the phase separation of the polymer solutions in the metastable state: (1) The temporal behavior of the phase separation can be divided mainly into two time regimes. (2) $R(t)$, $I_{2,0}(t)$, and $N(t)$ are described well by the power law relations with time in the respective time regime. (3) In the former time regime, $R(t) \sim t^1$, $I_{2,0}(t) \sim t^6$, and $N(t) \sim t^0$. (4) In the latter time regime, $R(t) \sim t^{1/3}$, $I_{2,0}(t) \sim t^1$, and $N(t) \sim t^{-1}$. (5) The crossover from the former to the latter regime is relatively sharp. (6) The minority phase grows faster with the increase of the quench depth.

The exponents for the latter regime are in good agreement with those expected for the coagulation (diffusion-reaction) of droplets, and this regime is the coarsening stage ascertained by the constancy of mass fraction of minority phase, NR^3 . Coarsening stage process was clearly observed. The coagulation is the dominant mechanism rather than the Ostwald-ripening one in case of solutions with high fluidity. It should be noted that the exponents for the time dependence are the same for both mechanisms. The former stage should be the growth stage succeeding to the nucleation stage which could not be detected clearly. An existence of the intermediate stage was not definitely observed. The coagulation may proceed much faster than the Ostwald ripening mechanism, and this fact could be the reason why the intermediate stage was not detected in the present work.

The t^{-1} growth of $R(t)$ is contrary to $t^{1/2}$ evolution predicted for the diffusion limited growth. That is, the growth mechanism in the present polymer solution is different from it. In the phase separation of dilute polymer solution, the minority phase is a concentrated phase and is in a highly entangled state. The mixing of polymer molecules with droplets needs a formation of entanglements and diffusion of polymer chains in the entangled network in the concentrated minority phase (droplets). According to de Gennes [3], the characteristic time τ_e for this process is evaluated as $\tau_e \sim a^2 P^3 \phi^{3/2} / D_1$ with a , P , ϕ , and D_1 being the unit monomer length, degree of polymerization, volume fraction of the polymer in the droplet, and diffusion coefficient of the monomer, respectively. Assuming $a \sim 0.25$ nm, $P \sim 6000$, $\phi \sim 0.18$, and $D_1 \sim 10^{-6}$ cm²/s from the phase diagram and literature values of PS, we obtain $\tau_e \sim 10$ s. On the other hand, the diffusional time τ_1 of a single polymer chain in the majority (dilute) phase is evaluated as $\sim R^2 / 6D_0$ with D_0 being the diffusion coefficient of a polymer chain. τ_1 is evaluated as 5 ms with $D_0 \sim 10^{-7}$ cm²/s and $R \sim 0.5$ μ m. Therefore, the mixing of the individual polymer chains forming the entanglements in the droplets (not the diffusion of polymer chain) is the limiting process. The surrounding environment of the droplets is constant in the present very dilute polymer solution. This means the constant flux and the growth of minority phase (droplet) is proportional to the surface area. As a result, $dR^3(t)/dt \sim R(t)^2$ and $R(t) \sim t^1$. The entanglements characteristic to the polymer system play an essential role in the phase

separation kinetics [4].

REFERENCES: [1] A. Cumming, P. Wiltzius, and F. S. Bates, Phys. Rev. Lett. 65, 863 (1990). [2] M. Tokuyama and Y. Enomoto, Phys. Rev. Lett. 69, 312 (1992). [3] P. G. deGennes, *Scaling Concepts in Polymer Physics* (Cornell Univ. Press, Ithaca, 1979). [4] H. Sato, N. Kuwahara, and K. Kubota, Phys. Rev. E 50, R1752 (1994).

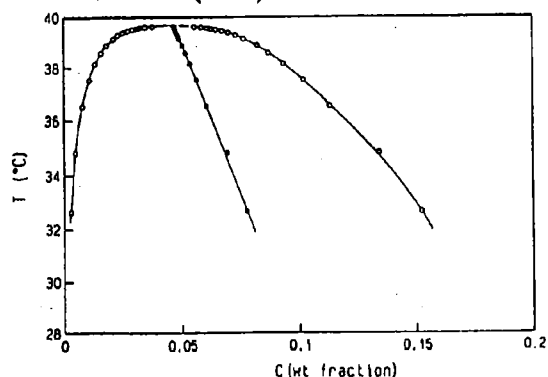


Fig. 1. Coexistence curve for PS ($M_w = 60.0 \times 10^4$) and DEO mixture. $T_c = 39.630^\circ\text{C}$ and $C_c = 4.66\text{wt}\%$.

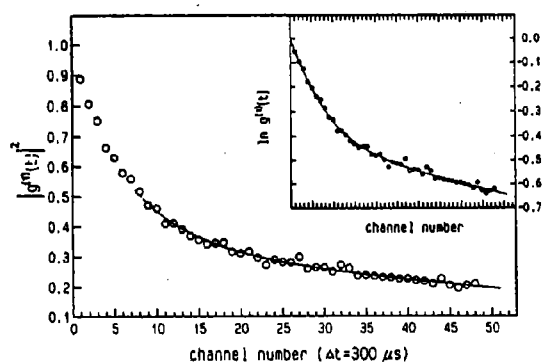


Fig. 2. Correlation function of PS/DEO (0.40mg/g) at the quench depth 0.10°C and 60 min after the quench. Dotted curve is the calculated one from eqs. 1 and 2.

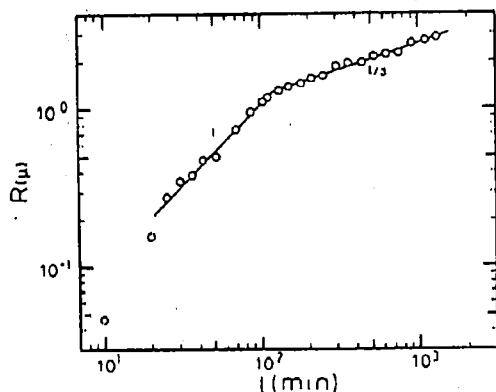


Fig. 5. $R(t)$ vs. t for PS/DEM (0.211 mg/g) at $\Delta T = 0.10^\circ\text{C}$.

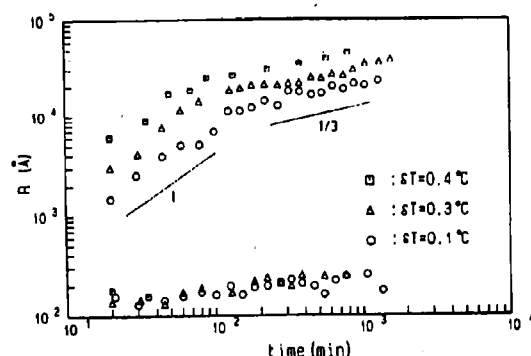


Fig. 3. Droplet radius $R(t)$ for PS/DEO as a function of the elapsed time. $\circ$, Δ , and $\square$ denote 0.10, 0.30, and 0.40°C of the quench depth. The lower data points correspond to individual polymer chain.

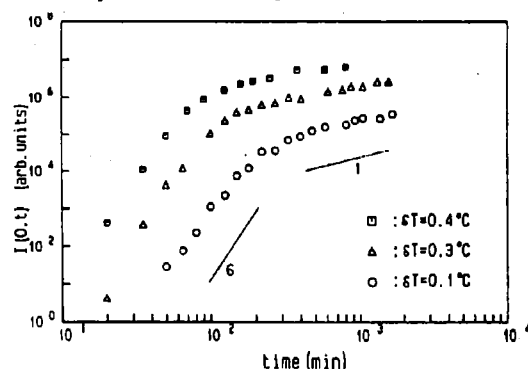


Fig. 4. Zero-angle scattered intensity vs. time. The symbols are the same as those in Fig. 3.

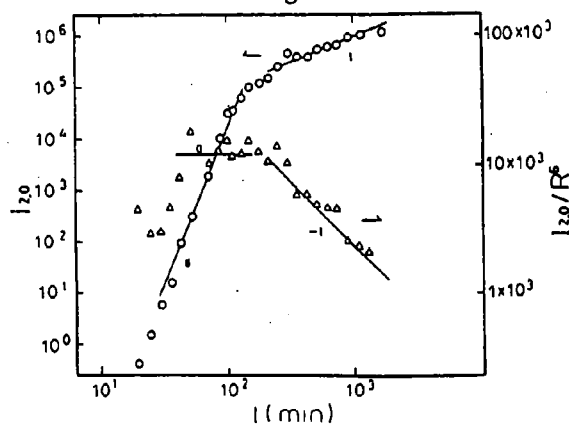


Fig. 6. Time dependence of zero-angle scattered intensity and number density of droplet for PS/DEM ($\Delta T = 0.10^\circ\text{C}$).