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Later-stage spinodal decomposition in polymer solution under high pressure—analyses of q_m and I_m

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Abstract

Later-stage spinodal decomposition (SD) of polymer solutions (polypropylene/trichlorofluoromethane) induced by pressure-jump was examined in situ as a function of pressure P by using time-resolved light scattering method with the cell designed for high pressure and high temperature. The time-evolution of the magnitude of scattering vector $q_m(t,P)$ at maximum scattered intensity and the maximum scattered intensity $I_m(t,P)$ were analyzed in order to characterize the coarsening processes of the later-stage SD, where t refers to time after the onset of pressure-jump. The changes in $q_m(t,P)$ and $I_m(t,P)$ with t at different P's were found to fall onto the respective master curves on the reduced plots, indicating that the scaling postulate is valid not only for the coarsening behaviors at different temperatures but for those at different P's.

Keywords: Pressure jump; Later-stage spinodal decomposition of polymer solutions; LBM scaling postulate

1. Introduction

The dynamics of phase separation processes in polymer/(nearly) supercritical fluid systems has been a fascinating subject, since the polymer processing in supercritical fluids has been increasing importance to make high performance materials such as the formation of fine particles and porous media [1]. In our previous paper [2], we investigated the early stage spinodal decomposition (SD) of polymer solutions polypropylene (PP)/trichlorofluoromethane (CCl_3F) induced by pressure-jump with a light scattering instrument particularly designed for polymer solutions under high pressure and high temperature. The changes in the scattered intensity with time at the early stage SD can be approximated by linearized Cahn theory [3] or linearized Cahn-Hillirard-Cook theory [4]. We obtained the characteristic parameters in the early stage SD such as the inter-diffusion coefficient $D_{app}(P)$ at pressure P and the characteristic magnitude of scattering vector $q_m(0,P)$ at P and at time $t \cong 0$ from the analyses of the changes in the scattered intensity with the theories, where the magnitude of scattering vector q is defined by

$$q = \frac{4\pi}{\lambda} \sin\frac{\theta}{2} \tag{1}$$

with λ and θ being, respectively, the wavelength of the incident beam and the scattering angle in the medium.

In this paper, we shall focus on the later-stage SD in PP/CCl_3F after the early stage SD. Many experimental studies [5–22] were reported on the coarsening processes in the later-stage SD of polymer mixtures, polymer solutions, and simple liquid mixtures by using scattering methods. In the later-stage SD the nonlinearity in the time evolution of the amplitude of the concentration fluctuations becomes increasingly important, and the phase-separated structure coarsens with time. The coarsening behaviors in the later-stage SD are characterized by the time evolution of the magnitude of scattering vector $q_m(t)$ at maximum scattered intensity and the maximum scattered intensity $I_m(t)$ at time t. Time evolutions of $q_m(t)$ and $I_m(t)$ are expressed by the following scaling laws:

$$q_m(t) \sim t^{-\alpha} \tag{2}$$

and

$$I_m(t) \sim t^{\beta} \tag{3}$$

The later-stage SD can be divided into intermediate stage and late stage [23]. In the intermediate stage SD, both the amplitude and the wavelength of the concentration fluctuations increases

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with time. On the other hand, in the late stage SD, the interfaces between two coexistence phases are well developed and the local concentration of each component in the domains reaches its equilibrium value. Although the amplitude of the concentration fluctuation has reached its equilibrium values, the size of the domains are still growing to reduce the excess free energy associated with the interfacial area. The scaling exponents β and α in the intermediate stage exhibits the relationship of

$$\beta > 3\alpha \tag{4}$$

while the relationship changes into

$$\beta = 3\alpha \tag{5}$$

in the late stage. The change, thus, allows us to distinguish the intermediate stage from the late stage. Furthermore, we found that the late stage can be divided into late stage I and II from the scaling law of the time-evolution of the interfacial area density [18,19].

Previous studies of the later stage SD have focused on test of scaling postulate proposed by Langer, Bar-on, and Miller [24,25] (LBM) on the time changes in $q_{\mathrm{m}}(t)$ and $I_{\mathrm{m}}(t)$. According to LBM scaling postulate, the reduced variables Q_{m}, $\tilde{I}_{\mathrm{m}}$, plotted as a function of the reduced time τ becomes universal, where

$$Q_{\mathrm{m}}(\tau) = \frac{q_{\mathrm{m}}(\tau)}{q_{\mathrm{m}}(0)} \tag{6}$$

$$\tilde{I}_{\mathrm{m}}(\tau) = \frac{I_{\mathrm{m}}(\tau) q_{\mathrm{m}}^3(0)}{\int_{q'}^{q''} q^2 I(q,\tau)\mathrm{d}q} \tag{7}$$

and

$$\tau = \frac{t}{t_{\mathrm{c}}} \tag{8}$$

with q' and q'' being the lower and upper bounds of the wave number q beyond which $q^2 I(q,\tau)$ in Eq. (7) becomes effectively zero. Here the characteristic time t_{c} is given by

$$t_{\mathrm{c}} = [q_{\mathrm{m}}^2(0) D_{\mathrm{app}}]^{-1} \tag{9}$$

The previous studies [6,11–14,18,20,26] have proven the LBM scaling postulate is valid for a range of temperatures covered.

In this paper, we will report results of our investigation on the phase separation processes of the later-stage SD in the PP/$\mathrm{CCl_3F}$ with the time-resolved light scattering. We shall check the existence of the crossover behavior from the intermediate stage to late stage in the coarsening behavior and confirm whether or not the previous observations and conclusions obtained for temperature-jump experiments is valid for the SD processes of the PP/$\mathrm{CCl_3F}$ obtained for the pressure-jump.

2. Experimental section

2.1. Light scattering instrument

As described in our previous paper [2,27], the light scattering instrument used in this study has the following features: (1) the instrument withstands up to pressure 34.3 MPa and temperature 573 K; (2) viscous polymer solutions can be easily handled; (3) pressure jump can be attained with 0.01 MPa precision, and (4) the scattered intensity distribution over wide angular range (0–30° in the air) can be measured at 100 scans/s by using the photodiode array light scattering system. We describe below only the essential part of the apparatus for this work and the details should be referred to the reference [2,27].

2.2. Sample preparation and quench condition

The polymer and solvent used here are, respectively, PP (weight-average molecular weight $M_{\mathrm{w}} = 3.5 \times 10^5$, $M_{\mathrm{w}}/M_{\mathrm{n}} = 6.5$, M_{n}: number-average molecular weight) and $\mathrm{CCl_3F}$. The solution has lower critical solution temperature and upper critical solution pressure type phase diagram. The phase diagram of the solution in the parameter space of P and weight fraction (w) at 452.5 K used in this experiment is reported in our previous paper. The polymer solution containing 1.5 wt% of the polymer was used for this study. We stirred the polymer solution at 453 K and 10 MPa for 30 min. to make the solution homogeneous and then kept the solutions at temperature $T =$ 452.5 K and $P = 4.90$ MPa before we quenched the solution from $P = 4.90$ to 4.78 ($\Delta P = 0.1$), 4.73 ($\Delta P = 0.15$), 4.71 ($\Delta P =$ 0.17), and 4.67 ($\Delta P = 0.21$) MPa, where $\Delta P = P_{\mathrm{c}} - P$ with the cloud point pressure $P_{\mathrm{c}} = 4.88$ MPa.

The changes in the scattered intensity $I(q,t)$ at t and q after the onset of the pressure-jumps with time were measured by the photodiode array light scattering system. The scattered intensity was corrected for the fluctuation of the incident beam and the turbidity of the sample. The vapor–liquid equilibrium pressure at $T = 452.5$ K is 3.60 MPa.

3. Experimental results

Fig. 1 shows the time changes in the scattered intensity after the onset of pressure jump from $P = 4.90$ MPa to $P = 4.71$ at 452.5 K. Here the scattered intensity is plotted as a function of q. In the early stage SD or at $0.023 < t < 0.116$ s, the scattered intensity increases with time at observed q-region, subsequently the peak in the scattered intensity appears at the high q-region. The early stage SD have been already analyzed in our previous paper and the linearized theories can well describe the behavior of the scattered intensity as a function of time. In the later stage SD, the peak intensity $I_{\mathrm{m}}(t,P)$ at given P further increases with t and $q_{\mathrm{m}}(t,P)$ shifts towards smaller q with t, reflecting the coarsening processes occurs in the later-stage SD.

4. Analyses and discussion

4.1. Scaling analyses of $q_m(t,P)$ and $I_m(t,P)$

Figs. 2 and 3 show the time changes in $q_{\mathrm{m}}(t,P)$ and $I_{\mathrm{m}}(t,P)$, respectively, at various P's in the later-stage SD plotted as a function of t in the double logarithmic scale. The lower

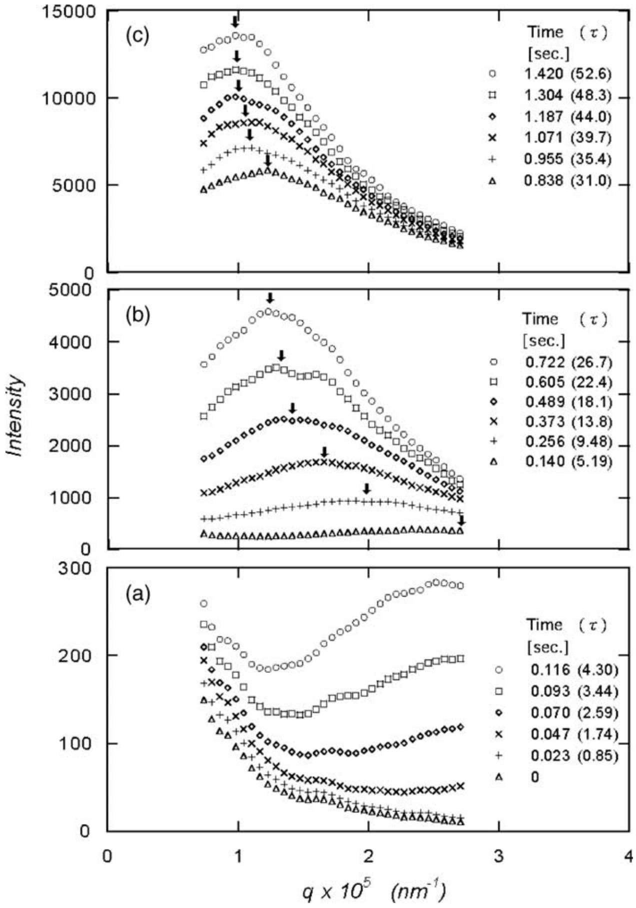

Fig. 1. Time change in the scattered intensity $I(q,t)$ plotted as a function of q after the onset of pressure jump from 4.90 to 4.71 MPa at 452.5 K. Time elapses in the order of (a)–(c). The part (a) covers the profiles from 0 to 0.116 s, (b) from 0.140 to 0.722 s, and (c) from 0.838 to 1.420 s after the onset of pressure jump. τ is the reduced time defined by Eq. (8).

the pressure P or the deeper the quench depth, the faster the growth of the phase-separated structure, thus giving rise to smaller $q_{\mathrm{m}}(t,P)$ and higher $I_{\mathrm{m}}(t,P)$ at a given t. Since the plots for each quench show some curvature, the exponents α and β depend on t. The arrows on the plot for $P=4.67$ and 4.71 MPa indicate the crossover time t_{cr} from the intermediate stage to late stage. This crossover time was determined from the crriteria given by Eqs. (4) and (5). For the other quench

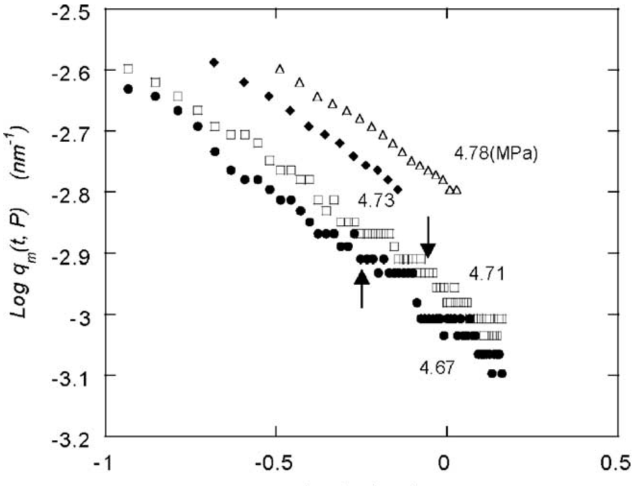

Fig. 2. Changes in $q_{\mathrm{m}}(t,P)$ with t at various pressures in double logarithmic scale. The arrows indicate the crossover time from the intermediate to late stage.

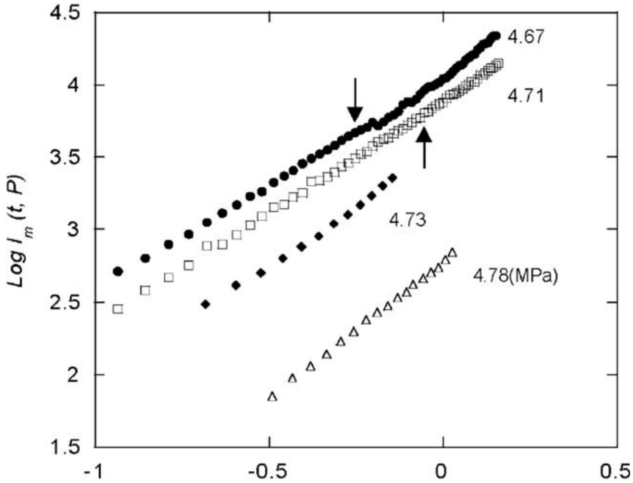

Fig. 3. Changes in $I_{\mathrm{m}}(t,P)$ with t at various pressures. The arrows indicate the crossover time from the intermediate to late stage.

Table 1
Scaling exponents at long time limit and crossover time

P (MPa)	α	β	β/α	t_{cr} (s)	τ_{cr}
4.78	0.39	1.87	4.79	–	–
4.73	0.40	1.77	4.42	–	–
4.71	0.54	1.63	3.00	0.89	32.8
4.67	0.59	1.77	3.00	0.56	34.9

condition, we do not find the crossover time, since $\beta > 3\alpha$ holds within the observed time region. Unfortunately, we can not determine the crossover time from late stage I to late stage II, since we were not able to analyze the time-evolution of the local structure due to the lack of the wide range of q. The scaling exponents at long time limits covered in this experiments and the crossover time are summarized in Table 1. The value of α increases with decreasing P. $\beta/\alpha = 3$ was found for $P = 4.67$ and 4.71 MPa, while $\beta/\alpha > 3$ was found for $P = 4.73$ and 4.78 MPa. This fact indicates that the phase separation processes at $P = 4.67$ and 4.71 MPa reaches the late stage SD where the amplitude of the concentration fluctuations reaches its equilibrium value and the wavelength of the concentration fluctuations grows with self-similarity but that the phase separation processes at $P = 4.73$ and 4.78 MPa have not reached yet during the observed time domain.

4.2. Test of the scaling postulate

We shall check whether the LBM scaling postulate [24,25] is valid for the coarsening processes at various P's. Table 2 summarizes the characteristic parameters obtained from the previous study in the early stage SD [2]. Figs. 4 and 5 show, respectively, Q_{m} vs. τ and $\tilde{I}_{\mathrm{m}}$ vs. τ. Each plot of Q_{m} and $\tilde{I}_{\mathrm{m}}$ at various P falls onto the respective master curves, indicating that LBM scaling postulate is valid for the phase separation process at various P's. Thus, pressure affects the time scale [through $t_{\mathrm{c}}(P)$] and the length scale [through $q_{\mathrm{m}}(0,P)$] in the coarsening processes but the mechanism of the coarsening processes is not affected by the change in pressure. This results is consistent with various experimental result obtained for T-jump experiments [8,11,12,14,18,20,28]. The arrows in Figs. 4 and 5 correspond to the crossover reduced time τ_{cr} from the intermediate to late stage given by

$$\tau_{\mathrm{cr}} = \frac{t_{\mathrm{cr}}(P)}{t_{\mathrm{c}}(P)} \tag{10}$$

Table 2
Parameters characterizing the early stage SD

P (MPa)	$D_{\mathrm{app}}(P) \times 10^6$ (nm^2/s)	$q_{\mathrm{m}}(0,P) \times 10^3$ (nm^{-1})	t_{c} (s)
4.78	1.57 ± 0.03	2.24 ± 0.04	0.126
4.73	2.16 ± 0.01	2.73 ± 0.02	0.062
4.71	3.50 ± 0.13	3.25 ± 0.12	0.027
4.67	4.23 ± 0.16	3.84 ± 0.15	0.016

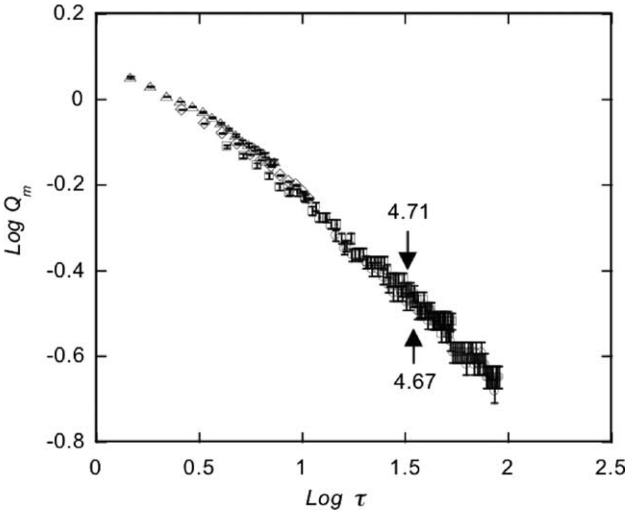

Fig. 4. Reduced wave number Q_{m} is plotted as a function of reduced time τ in double logarithmic scale. The arrows indicate the crossover reduced time from the intermediate to late stage.

We found that τ_{cr} is, respectively, 32.8 and 34.9 for $P = 4.71$ and 4.67 MPa and almost independent of P as shown in Table 1, which agrees with other experimental results [11,18,20,29]. We summarize below crossovers of the coarsening behavior:

(i) intermediate stage ($2 < \tau < \tau_{\mathrm{cr}}$)

$$\alpha = 0 - 0.4, \quad \beta = 1.27 - 1.20 \tag{11}$$

(ii) late stage ($\tau_{\mathrm{cr}} < \tau$)

$$\alpha = 0.4 - 0.6, \quad \beta = 1.20 - 1.80 \tag{12}$$

It should be noted that the crossover reduced time from the early stage to the intermediate stage is 2 where the time change

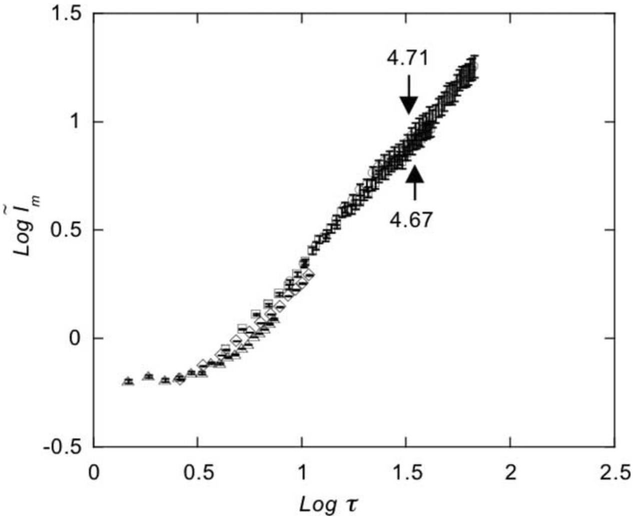

Fig. 5. Reduced peak intensity $\tilde{I}_{\mathrm{m}}$ is plotted as a function of reduced time τ in double logarithmic scale. The arrows indicate the crossover reduced time from the intermediate to late stage.

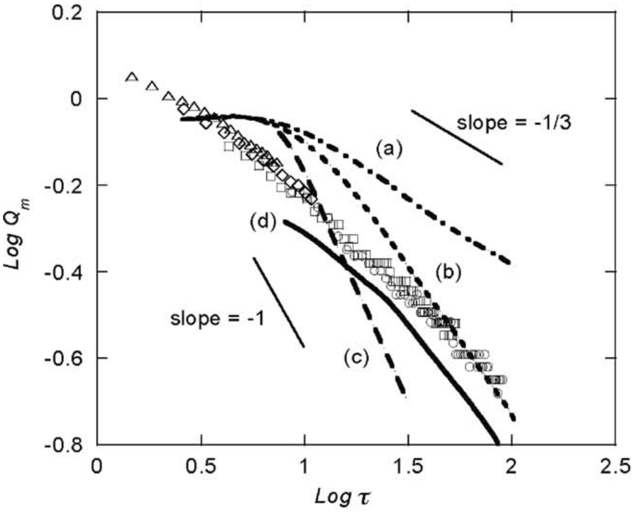

Fig. 6. Comparison of Q_m with those of computer simulation [(a)–(c)] by Koga and Kawasaki [37] and of simple liquid mixture (d) by Wong and Knobler [41]. (a) Q_m for the coarsening processes without hydrodynamic interactions, (b) Q_m for the coarsening processes where hydrodynamic interactions affects the coarsening, (c) Q_m for the coarsening processes where hydrodynamic interactions is dominant, (d) Q_m obtained for isobutyric acid/water system.

in the scattered intensity starts to deviate from that described by the linearized Cahn-Hillirad-Cook theory [2].

4.3. Comparison of Q_m

Fig. 6 shows the comparisons between our Q_m and those of computer simulation and other experiments. For the mixture at critical composition, the theory [30] and computer simulation [30–37] give $\alpha = 1/3$ for the mixture without hydrodynamic interactions, while they give $\alpha = 1$ for the mixture where the hydrodynamic interactions is dominant [22,31,37–40]. α at long time limit in our experiment is 0.6 and between 1/3 and 1, indicating that the hydrodynamic interactions have affected the coarsening behavior but have not yet been dominant in the observed time domain. The exponent $\alpha = 1$ is expected to be observed at the time scale longer than the observed time domain. Our result was compared with those of the computer simulation for solid case (line a) where the hydrodynamic interactions is absent, viscous case (line b) where the hydrodynamic interaction affects the coarsening behavior, and fluid case (line c) where the hydrodynamic interactions is dominant. At a long time limit, our result is in good agreement with that given by line b, indicating that the hydrodynamic interaction have affected the coarsening behavior in the polymer solution. We also compared our results with that of isobutyric acid/water system by Wong and Knobler [41] (line d). Although the similar tendency in Q_m is observed in both system but our experimental curve shifted to longer time region. This shift may be due to the entanglements of polymers, since the number of the entangle points can not be scaled with $t_c(P)$, which has been already discussed theoretically by Onuki [42] and by Koga-Kawasaki [37] as well as experimentally in our previous papers [11,29].

5. Conclusion

The later-stage SD of PP/CCl_3F induced by pressure-jump was examined in situ as a function of P by using time-resolved light scattering method. In the later-stage SD, the peak intensity $I_m(t,P)$ increases and $q_m(t,P)$ shifts towards smaller q with t, reflecting the coarsening processes occurs in the later-stage SD. The time-evolution of $q_m(t,P)$ and $I_m(t,P)$ were expressed by the scaling laws: The changes in $q_m(t,P)$ and $I_m(t,P)$ with t at different P's were found to fall onto master curves on the reduced plots, indicating that the scaling postulate is valid for the coarsening behaviors at different P's.

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