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Kinetics of phase separation by spinodal decomposition in a liquid-crystalline polymer solution

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Time-resolved light scattering studies have been undertaken for elucidating the dynamics of phase separation in aqueous HPC (hydroxypropyl cellulose) liquid-crystalline solutions. The HPC/water system phase separates during heating and returns to a single phase upon cooling. The phase diagram of thermally induced phase separation was subsequently established on the basis of cloud point measurements. For kinetic studies, T (temperature) jump experiments of 10 per cent aqueous HPC solutions were undertaken. Phase separation occurs in accordance with the spinodal decomposition mechanism. At low T jumps or in reverse quenched experiments, the scattering maximum remains invariant as predicted by the linearized Cahn-Hilliard theory. However, at large T jumps, the SD is dominated by non-linear behaviour in which scattering peaks move to low scattering angles. The latter process has been identified to be a coarsening mechanism associated with the coalescence of phase separated domains driven by a surface tension. A reduced plot has been established with dimensionless variables Q and τ . It was found that the scaling law is not valid over the entire spinodal process. The time evolution of the scattering profiles of 10 per cent HPC solutions, following a T jump to 49°C, is tested with the scaling law of Furukawa. It seems that the kinetics of phase separation at 10 per cent solution resemble the behaviour of off-critical mixture.

1. Introduction

The phenomenon of phase separation in liquid-crystalline polymer solutions is a relatively new field of interest. Phase equilibria of rigid rod macromolecules have been first introduced by Flory [1] who predicted that phase separation of rod-like molecules may occur in athermal solutions in a manner dependent upon the volume fraction of rods, the axial ratio of rods and the polymer-solvent interaction. The effect of chain flexibility has also been incorporated in his thermodynamic treatment.

In general, phase separation phenomenon in liquid-crystalline polymer solutions has been complicated by additional factors such as phase transitions, gelation and the presence of superstructure. Miller and co-workers [2, 3] found that PBLG (poly- γ benzyl L-glutamate) in DMF (dimethyl formamide) reveals phase behaviour (temperature-composition) covering both isotropic and anisotropic liquid-crystalline phase. When lyotropic solutions are brought into the biphasic region, gelation takes place and has been attributed to phase separation in the system. According to the authors [4], the mechanism by which phase separation occurs is not completely understood. However, their light-scattering studies show a strong increase of scattered intensity without movement of the peak position, suggesting the enhancement of the concentration gradient between the phases. This process is reminiscent of spinodal decomposition in binary mixtures [5] as will be discussed later.

Another kind of rigid-rod polymer which shows gelation associated with phase separation is the PBT (poly-*p*-phenylene benzobisthiazole) in a MSA (methane sulfonic acid) system [6]. This heterocyclic polymer, which was first synthesized at the Wright-Patterson Air Force Base, has been shown to have an ultrahigh modulus and extremely high strength. Phase separation in PBT-MSA systems was noticed by Helminiak and co-workers [6, 7]; nevertheless, it was not elaborated further. Phase equilibria of ternary system, namely, PBT/ABPBI [poly-2,5(6)benzimidazole] in MSA solutions, were also established and compared with Flory's thermodynamic theory [8] for ternary systems. The authors concluded that the equilibrium phase segregation behaviour could be modelled by the large disparity of the chain geometry and the rigidity of the two polymer components involved. Recently, phase separation induced gelation in PBT-sulphuric acid was reported by Russo *et al.* [4].

Aqueous hydroxypropyl cellulose (HPC in water) is another type of rodlike material reported to undergo phase separation during heating. HPC is a semicrystalline polymer in the solid state [9] but exhibits thermotropic liquid-crystalline character in the mesomorphic state. It reveals isotropic phase in dilute aqueous solutions, but forms an ordered liquid-crystalline phase with a cholesteric structure in concentrated solutions [10]. Werbowyj and Gray [11] observed that dilute solutions of HPC turned intense white on heating above 45°C. This behaviour has been attributed to phase separation between polymer-rich and -poor regions. A qualitative phase diagram of the HPC-water system was subsequently established and the thermodynamic aspect of phase equilibria was treated by incorporating the effect of chain flexibility. To the best of the authors' knowledge, the kinetic aspects of phase separation in rigid-rod molecular systems have not been treated adequately. This gap the present study seeks to address.

In the present paper, time-resolved light scattering has been employed for the elucidation of kinetics of phase separation in aqueous hydroxypropyl cellulose. The study has been focused on the establishment of phase equilibria and on the temperature jump experiments at low concentrations. The results are interpreted in terms of spinodal decomposition mechanisms [12-21].

2. Experimental

The hydroxypropyl cellulose used in this study was HPC-E with a molecular weight $M_w \approx 60,000$, kindly supplied by Hercules Incorporated. Various aqueous HPC solutions, typically from 1 to 80 per cent concentrations, were prepared by dissolving it in distilled water. Concentrated solutions were obtained by evaporating dilute solutions and the percentage concentration was calculated on the basis of weight change. The solutions were sealed in a demountable cell (Wilmad Glass Co., model WG-20/C) of 1 mm and in some cases 0.1 mm path length. The total weight of photocell and solutions was measured before and after light scattering experiments to assure that the cell was properly sealed.

A time-resolved light scattering set-up, schematically shown in figure 1(a), was used. It consists of a laser light source (He-Ne laser with a wavelength of 6328 Å), a set of polarizer and analyser, a sample hot stage and screen. Scattered patterns from polymers may be photographed using a Polaroid instant camera (Polaroid Land Film Holder 545). The scattered intensity can be quantitatively monitored by means of a two-dimensional Vidicon camera (1254 B, EG&G Co.) coupled with a detector controller (model 1216, EG&G Co.). The analogue signal is digitized and analysed on an OMA III (Optical Multichannel Analyzer) system. The scan rate is typically

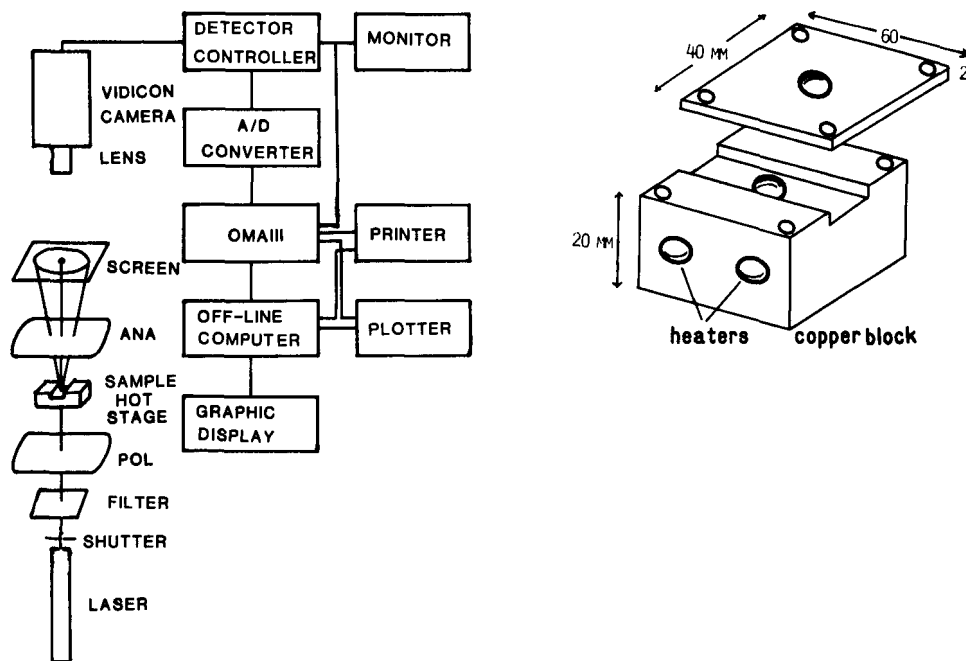


Figure 1. (a) Schematic diagram of time-resolved light scattering set-up and (b) a sample hot stage.

30 ms for a one-dimensional scan and about 0.5 to 1.5 s for a two-dimensional mode depending on the number of pixels chosen for grouping. Various modes of data acquisition are available for selection commensurate with experimental configurations. The raw data are further transferred to an off-line computer (IBM-XT) for post data treatments such as background correction, data smoothing, rescaling, etc. Generally, a set of sample hot stages is used for temperature jump studies; one is controlled at an experimental temperature and the other is preheated below phase separation points. The schematic drawing of the hot stage is depicted in figure 1(b). Various T jump experiments from room temperature to 46°, 47°, 49°, 50° and 52°C were undertaken for 10 per cent solutions. One T quench experiment was carried out from 46°C to 45°C.

3. Results and discussion

3.1. Phase equilibria

The 10 per cent aqueous HPC solution was sealed in a demountable cell of 1 mm path length. The solution was initially transparent and scattered no light. When the solution was heated in a sample hot stage, the sample turned white in the vicinity of 46°C. Interconnected domains were observed in the optical microscopic investigation. In small-angle light scattering studies, a diffuse light scattering halo developed and collapsed to smaller diameters with continued heating. This SALS halo was obtained without using any polarizers. There is no H_v (horizontal polarizer with vertical analyser) in such dilute HPC solutions either in a single phase or biphasic regime. The V_v (vertical polarizer with vertical analyser) pattern is reminiscent of the SALS halo without using the polarizers. This suggests that the V_v scattering arises exclusively from concentration or density fluctuations rather than the orientation fluctuations. A typical scattering image of the 10 per cent HPC solution obtained at 47°C is depicted

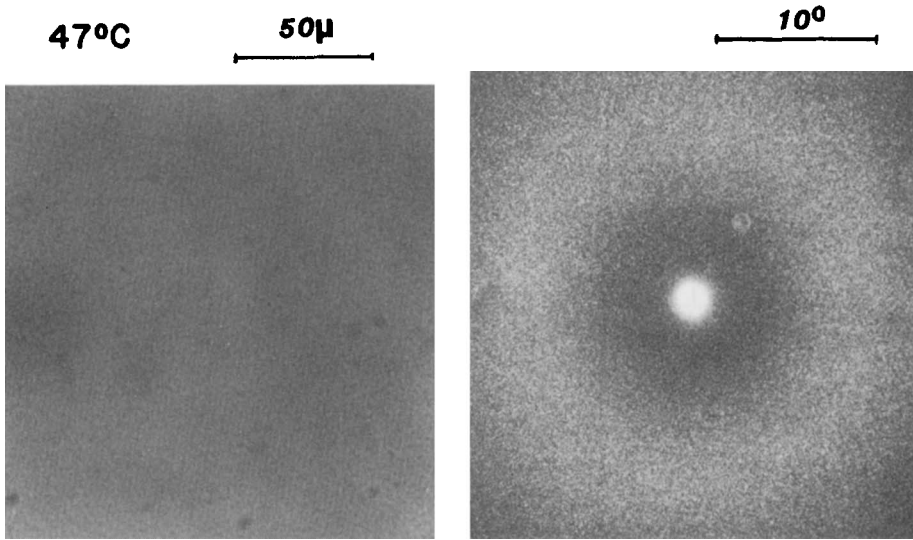


Figure 2. Optical micrograph showing interconnected domains of 10 per cent HPC solution at 47°C and the corresponding scattering halo characterizing spinodal decomposition.

in figure 2 along with the corresponding optical micrograph. A diffuse SALS halo and high level of interconnectivity of phase separated domains are the familiar characteristics of spinodal decomposition [12–18].

The process of phase separation in HPC solutions can be quantitatively monitored during the course of heating using time-resolved light scattering mentioned previously. Figure 3 shows the evolution of scattering curves obtained at a heating rate of 2°C/min. The scattering maximum first develops around 47°C and the peak shifts toward low scattering angles, characterizing the phase growth. Upon cooling, the scattering peak diminishes without accompanying any movement of the peak

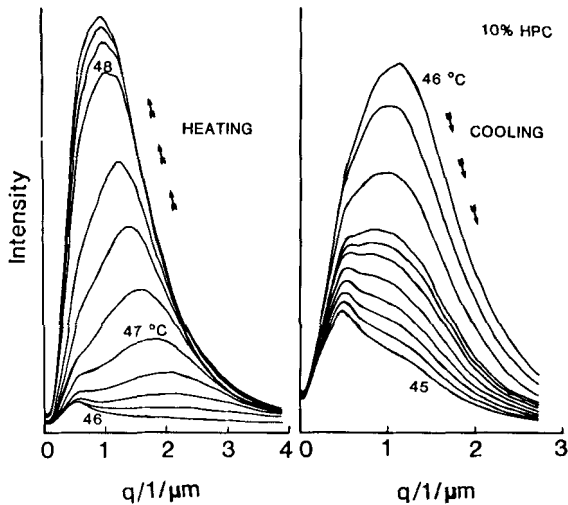


Figure 3. The evolution of scattering curves of the 10 per cent aqueous HPC as a function of temperature during heating and cooling. The heating rate was 2°C/min. and the cooling rate was 0.2°C/min.

position. This is associated with phase dissolution in which the two-phase system transforms to a single phase. The domain size remains unchanged, but the concentration gradient decreases during cooling. Visually, the white HPC solution turns transparent.

We now turn our attention to the establishment of the cloud point phase diagram. In conventional cloud point determinations by light scattering, the change of scattered intensity is monitored at an arbitrary angle. There is no general rule to such a choice, but is commonly measured at a wide scattering angle in order to detect the early stage of phase separation. In the present case, the scattering peak moves to low scattering angle during phase separation, hence, the intensity is monitored at an angle where the scattering maximum first develops. Incidentally, it corresponds to the scattering wave numbers (q) of $3.1 (1/\mu\text{m})$. Figure 4 shows the variation of scattered intensity at $q = 3.1$ as a function of temperature. The intensity is initially constant but changes drastically at a particular temperature. The cloud point is taken as the temperature at which the change of slope occurs.

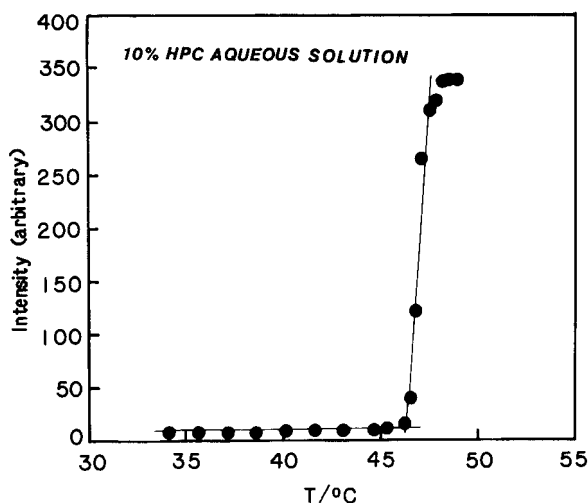


Figure 4. The variation of scattered intensity with temperature monitored at wave number $q = 3.1 (1/\mu\text{m})$.

The cloud point phase diagram was subsequently established and depicted in figure 5. This phase diagram is apparently different from that of Werbowyj and Gray [11], in particular near the 50 to 60 per cent HPC concentrations in which the cholesteric structure persists through out the phase separation process. Our phase diagram resembles an LCST (lower critical solution temperature), but reveals a discontinuity near the 50 to 60 per cent concentrations. The higher concentration curve is similar to that reported by Nishio *et al.* [22], while the lower concentration curve is reminiscent of that of Werbowyj and Gray [11]. At low concentrations, phase separation occurs by a spinodal process; however, gelation seems to occur during phase separation in the high concentration regime. Basically, our phase diagram of the HPC-water system of the three distinct regions: (1) isotropic region at low concentrations; (2) anisotropic colour regime with cholesteric liquid-crystalline structure at intermediate concentrations; and (3) gelation region at high concentrations. The behaviour of phase separation seems very complex at the latter two regimes because complex superstructures are present in the system throughout the phase

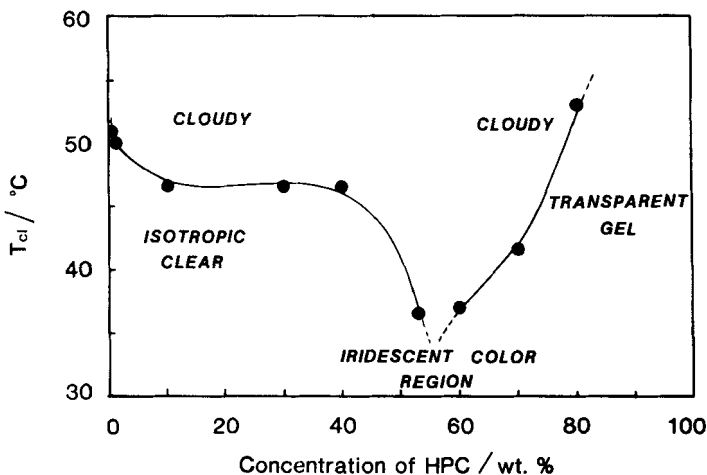


Figure 5. A cloud point phase diagram of aqueous HPC solution obtained at a heating rate of $2^\circ\text{C}/\text{min}$.

separation process. Hence, we focus our attention only on the simplest isotropic cases for kinetic study.

3.2. Early stages of spinodal decomposition

Figure 6(a) and (b) exhibit time evolution of scattering curves of the 10 per cent aqueous HPC obtained at a T jump from room temperature of 46°C and reverse quench from 46° to 45°C . The scattering maximum appears at around $q = 3.1$ ($1/\mu\text{m}$) during the T jump, and the peak position remains stationary while the intensity increases immensely. In the reverse quenched experiments, the scattered

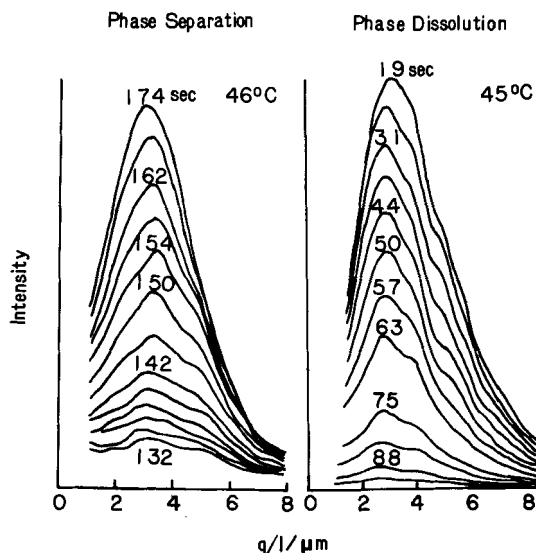


Figure 6. Time evolution of scattering curves of the 10 per cent aqueous HPC solution following a temperature jump from room temperature to 46°C , and a reverse quenched from 46° to 45°C .

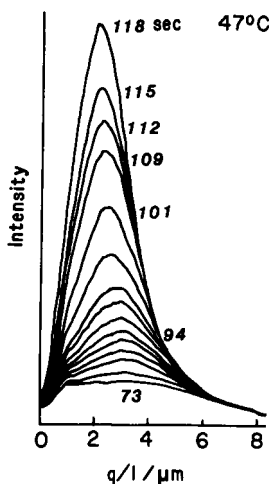


Figure 7. Time evolution of scattering curves of the 10 per cent aqueous HPC solution following a temperature jump from room temperature to 47°C.

intensity decayed with time without accompanying any movement of the peak position. This tendency has been observed in larger quench depths; the details are reported in a separate paper [23]. This behaviour is exactly what was predicted in the linear theory of Cahn–Hilliard. However, at large T jumps to 47°, 49° and 52°C, the scattering peak moves to lower scattering angles very rapidly, and hence the early stage of SD is not clearly observed (figure 7). We believe that the general trend of phase separation in the aqueous HPC is non-linear; however, there is an appreciable period at which the scattering peak remains constant, in particular at a low T jump of 46°C. In this regime, the phase separated domains are not getting larger, but merely the concentration gradient at the phase boundaries becomes larger. This observation is in conformity with the prediction of the linear theory, and hence is worthy of testing with the linearized Cahn–Hilliard equation which predicts the exponential growth of scattering intensity, i.e.

$$I(q, t) = I(q, t = 0) \exp \{2R(q)t\}, \quad (1)$$

where t is the phase separation time and q is the wave number being equal to $(4\pi/\lambda) \sin(\theta/2)$. Here, λ and θ are respectively the wavelength of light and the scattering angle measured in the medium. The amplification factor $R(q)$ which characterizes the growth process is further related by

$$R(q) = -Mq^2 \{(\partial^2 f / \partial c^2) + 2\kappa q^2\}, \quad (2)$$

where f is the local free energy, c represents the concentration, κ is the composition gradient coefficient and M is the mobility. $R(q)$ is a quantity that can be measured experimentally according to equation (1).

Figure 8(a) shows a plot of logarithmic scattered intensity as a function of time for various wave numbers. As predicted by the linearized theory, there is a period where $\log I$ varies linearly with t . However, at a later time, the intensity deviates from the linear slope and levels off. The amplification factor $R(q)$ was evaluated from the initial slope. The value of $R(q)/q^2$ is then plotted against q^2 in figure 9 to test with the linearized theory (equation (1)). As can be seen in figure 9, the plots of $R(q)/q^2$ versus q^2 seem linear for low T jumps, but appreciable deviations are seen at large T

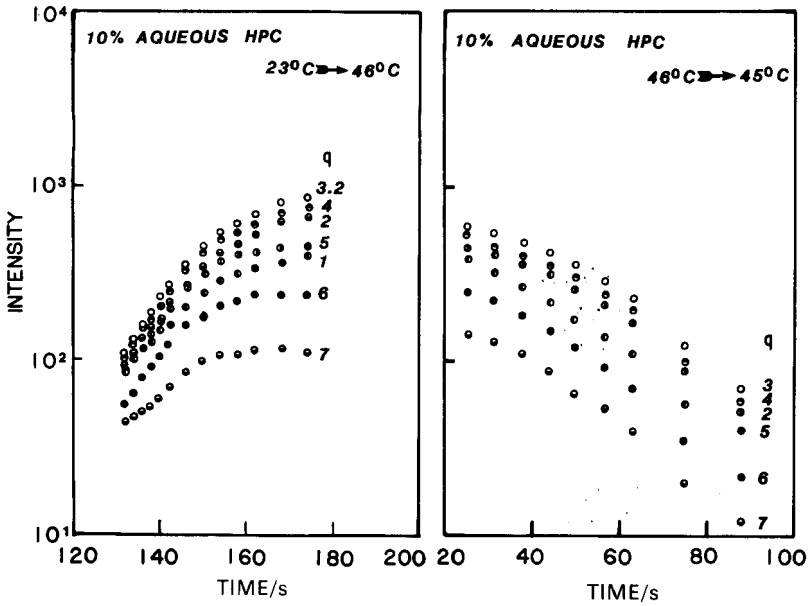


Figure 8. (a) The change of logarithmic scattered intensity versus time (s) for various wave numbers following a T jump to 46°C and (b) a reverse quench to 45°C .

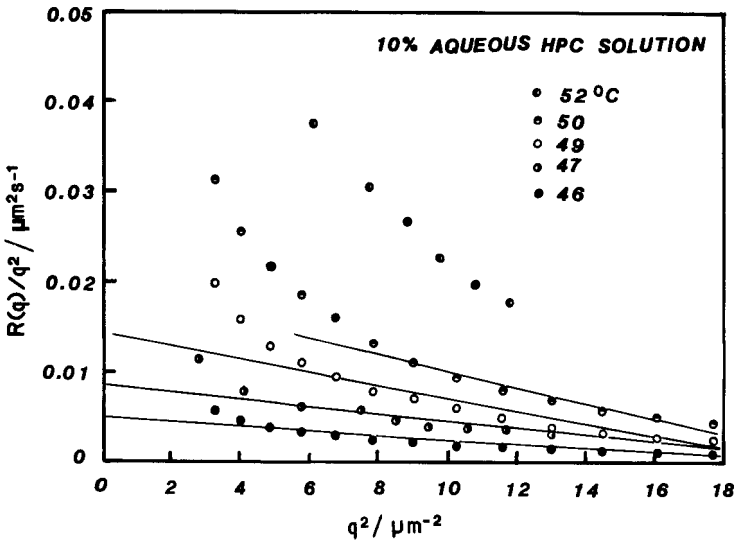


Figure 9. The plots of $R(q)/q^2$ versus q^2 for various T jumps of the 10 per cent aqueous HPC.

jumps probably because of the contribution from the coarsening or the late stage of spinodal decomposition. In a reverse quench experiment from 46°C to 45°C shown in figure 6(b) the scattering peak decays with time, but the peak position remains stationary. The semilogarithmic plot of scattered intensity with phase dissolution time in figure 8(b) appears linear as predicted by the linear theory. However, except for a few cases in polymer blends [24, 25] a majority of studies [26–28] on the spinodal decomposition shows the inadequacy of the linearized Cahn–Hilliard theory.

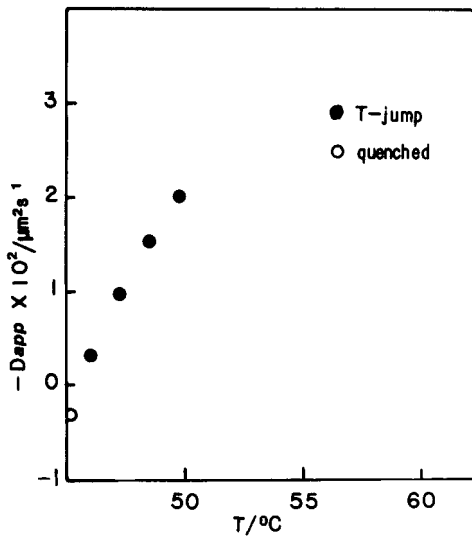


Figure 10. Apparent diffusion coefficients as a function of temperature showing a spinodal temperature.

In the present case, the data at large T jumps are effected by the contribution from the late stages of SD, therefore deviate from linear relation particularly at small q . Hence, slopes were drawn through points at large q in conjunction with the relation $q_m^2 = q_c^2/2$, where q_c is the crossover wave number at which $R(q)$ becomes zero. The apparent diffusion coefficient $D = M(\partial^2 f / \partial c^2)$ was determined from the intercept in accordance with equation (2). The values are further plotted as a function of temperature in figure 10, together with the data obtained from a reverse quench experiment at 46°C. The temperature at which the apparent diffusivity becomes zero is commonly regarded as the spinodal temperature; incidentally it corresponds to 45.5°C in the present case.

3.3. Late stages of spinodal decomposition

The late stages of phase separation was treated by Langer *et al.* (LBM) [17] based on the non-linear statistical consideration. The LBM theory predicts the power law scheme for the late stage of SD. Binder and Stauffer (BS) [18] introduced a cluster theory in which the cluster aggregate and coalesce into larger domains associated with a decrease in free energy of the system. The BS theory predicts that the scaling law for the structure function $\tilde{S}(q, t)$,

$$\tilde{S}(q, t) = q_m^{-3} S(q/q_m), \quad (3)$$

holds as a result of the self-similarity of the microdomain structure. The subscript m represents the maximum value. According to the theory, the time evolution of the cluster size $r(t)$ has a simple form of the power law,

$$r(t) \propto t^\phi, \quad (4)$$

or in an equivalent expression,

$$q_m(t) \propto r(t)^{-1} \propto t^{-\phi}, \quad (5)$$

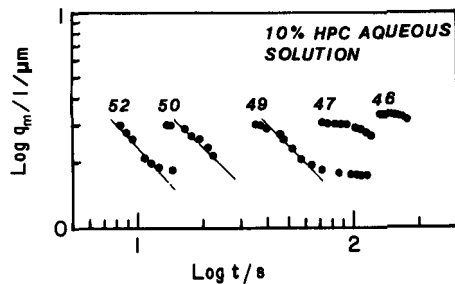


Figure 11. A log-log plot of maximum wave number (q_m) against phase separation time (t) for the 10 per cent aqueous HPC solution.

and

$$I_m(t) \propto r(t)^3 \propto t^\psi, \quad (6)$$

with $\psi/\phi = 3$ which results from the sum rule for the structure function, i.e. from the requirement that the composition of demixed phases remains unchanged with time.

As has been mentioned previously, the scattering peak shifts to low scattering angles in the late stages of spinodal decomposition, while the intensity continues to increase, characterizing the growth process. In accordance with equations (5) and (6), the wave number (q_m) and the intensity (I_m) were plotted against time in log-log plots. Figure 11 consists of three regions: (1) in the early period, the q_m is invariant with respect to time; (2) then the curves vary linearly with a slope of approximately -1 except for a shallow T jump at 46°C ; and (3) a change of slope occurs to smaller values at longer phase separation time. Figure 12 shows the variation of scattered intensity with time in that the slopes of $\log I_m$ versus $\log t$ are approximately 3, but deviate appreciably at a later time.

Since there is an appreciable period at which q_m is constant, the correlation length (ξ) is the single phase may be approximated as the initial fluctuation size of spinodal at the zero phase separation time, and may be expressed as

$$\xi = 1/q_m(t = 0). \quad (7)$$

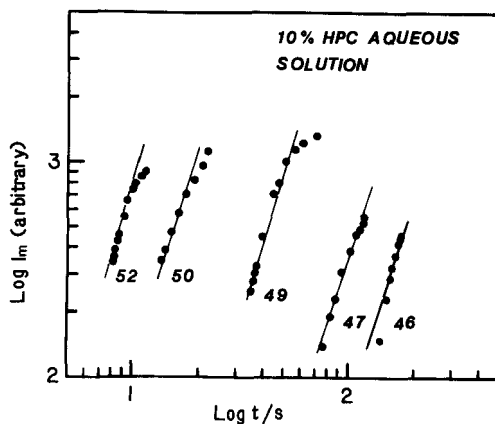


Figure 12. The corresponding log-log plot of maximum intensity (I_m) versus phase separation time (t) for the 10 percent aqueous HPC solution.

Then the scaling analysis was undertaken with reduced variables

$$Q = \xi q = q/q_m, \quad (8)$$

and

$$\tau = D\xi^{-2}t, \quad (9)$$

where the values of D for different T jumps can be determined in figure 8. The log-log plot of Q versus τ are depicted in figure 13. Now the data for various T jumps fairly fall on a single curve. This universal curve is comprised of three regions: (1) very short time (τ) or the early stages of spinodal decomposition, where Q is invariant; (2) later time where it exhibits a slope of -1 ; and (3) very late stages where it deviates considerably from -1 slope, i.e. the slope becomes smaller.

The first regime is nothing but the early stage of spinodal decomposition associated with the increase of concentration gradient as predicted by linearized Cahn-Hilliard theory. The second regime characterizes the late stage of spinodals where the power law schemes prevail. At high T jumps, the phase growth occurs linearly with time (i.e. slope of -1) which is exactly what was predicted by Siggia [19] for the coarsening process driven by surface tension. This mechanism has also been identified in the critical mixtures of some polymer blends or off-critical mixtures but with large T jumps. The small T jumps to 46°C shows a slope (about -0.4) appreciably smaller than -1 slope but somewhat larger than the $-1/3$ slope predicted for off-critical mixtures [18]. In the third region, the growth process seems to slow down. It is plausible that the interconnectivities break down to form droplets due to flow instability [29], but the droplets can coalesce again. The competition between the two processes seems important for the growth process of the very late stages of SD. Such behaviour was recently observed by Hashimoto in the blends of polyethylene terephthate (PET) and hydroxybenzoic acid-ethylene terephthate (PHB-PET) copolymer [30]. It seems the above scaling law is valid only in a limited period, but not operative over the entire phase separation process. This result is in good accord with the prediction of Kawasaki and Ohta [31] based on the hydrodynamic consideration.

3.4. Scaling of the structure function

As can be noticed from figure 5, no critical point is observed in the cloud point curves. Also most T jump experiments, except at 46°C , are deep quenches: thus it is hard to judge whether or not the kinetics of phase segregation at 10 per cent concentration follow the behaviour of critical or off-critical mixtures. It seems that the scaling law proposed by Furukawa [32] seems to be useful to differentiate this aspect. Furukawa suggested that in the low wave number region ($q < q_m$) the structure function $S(q)$ may have the form of

$$S(q < q_m, t) \propto q^2, \quad (10)$$

because of the conservation law of order parameter, whereas in the high q region ($q > q_m$), it may be represented by

$$S(q > q_m, t) \propto q^{-\gamma}, \quad (11)$$

where

$$\left. \begin{aligned} \gamma &= 2d, & \text{for the critical composition,} \\ \gamma &= d + 1, & \text{for the off-critical composition,} \end{aligned} \right\} \quad (12)$$

with d being the dimensionality of space. Combining equations (10) and (11). Furukawa obtained the following equation:

$$S(x) = \frac{(1 + \gamma/2)x^2}{\gamma/2 + x^{2+\gamma}}, \tag{13}$$

where $x = qr$. The shape of the structure function has been examined by Komura *et al.* [33] for metal alloys and Takahashi *et al.* [34] for polymeric mixtures using equations (10)–(13).

The time evolution of the scattering curves obtained at a T jump to 49°C was replotted in double logarithmic scale in figure 14. The slopes of 2 and -4 are shown

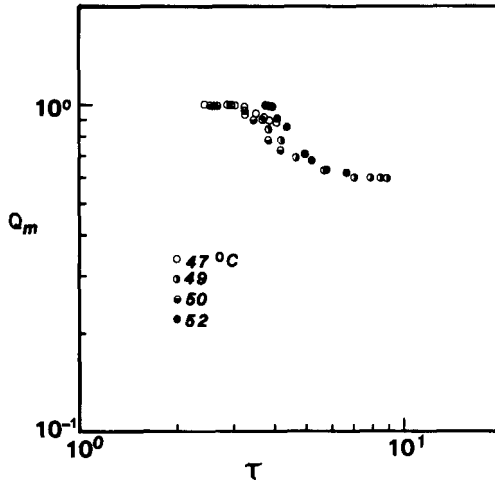


Figure 13. A reduced plot of dimensionless variables Q_m as a function of τ for the 10 per cent aqueous HPC solution.

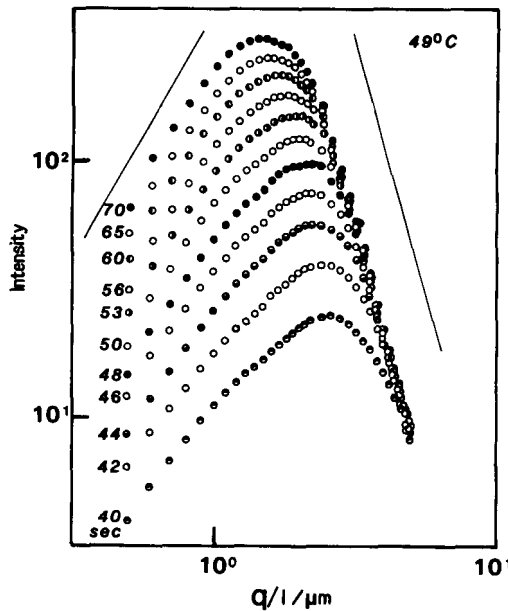


Figure 14. A double logarithmic plot of the time evolution of the scattering profiles following a temperature jump to 49°C .

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together for comparison purpose. As can be seen in figure 14, the shape of the intensity profile at the large q region ($q > q_m$) gives a slope of -4 , suggesting that the kinetic behaviour of 10 per cent HPC solutions is reminiscent of that of the off-critical mixtures. At small q regions ($q < q_m$), the slope of the scattering profile is slightly less than the predicted value of 2. This discrepancy may be associated with unreliability of the scattered intensity at small q regions because of the parasitic scattering arising from the beam stop. However, the scattering at large q regions is not affected by this parasitic scattering.

4. Conclusion

We have demonstrated that the phase separation mechanism in the 10 per cent aqueous HPC solution is the spinodal decomposition. At low temperature jumps, for example $\Delta T \sim 0.5^\circ\text{C}$, the scattering maximum remains constant with the evolution of time, while its magnitude increases immensely, as predicted by the linear theory of spinodal decomposition. However, at large temperature jumps, the scattering peak moves to low angles, thus the phenomenon of SD is dominated by the non-linear behaviour. A slope of $\phi = -1$ has been obtained as predicted by Siggia; this process has been identified to be the coarsening process driven by surface tension. The scaling law is not valid over the entire spinodal process. The kinetics of phase separation at the 10 per cent aqueous HPC solution resembles the behaviour of off-critical mixtures.

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