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Phase separation in aqueous poly(vinyl alcohol) solution

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Aqueous solutions of poly(vinyl alcohol) (PVA) were investigated by elastic and inelastic light scattering. In the initial stage of phase separation, a plot of the logarithm of scattered intensity against time formed a straight line when measurements were made in the sol region at less than the spinodal temperature estimated according to the method described by Cahn as being within the framework of linearized spinodal decomposition theory. No scattering pattern under Hv polarization conditions in the initial stage was observed for PVA gels prepared from aqueous solutions, apart from the X-type scattering pattern observed for PVA gels prepared from a dimethylsulfoxide/water mixture. This means that an aqueous solution of PVA does not form assemblies of crystallites such as rod-like and spherulitic textures in the phase-separation process. Hence the phase separation of aqueous solutions of PVA is apparently expected to be similar to that of amorphous polymer solutions due to spinodal decomposition. However, no definite scattering peak was observed as a function of scattering vector characterizing the latter stage of spinodal decomposition. Furthermore, in the initial stage, in the linear part of the plot of logarithm of scattered intensity against time, the decay rate estimated by inelastic light scattering decreased rapidly, indicating the progress of gelation. These contradictory phenomena indicated the possibility that the phase separation of aqueous PVA solutions is attributed to the simultaneous progress of spinodal decomposition and gelation.

(Keywords: poly(vinyl alcohol); light scattering; phase separation)

INTRODUCTION

It is well known that Zimm plots for aqueous poly(vinyl alcohol) (PVA) solutions show a curvature at room temperature. To avoid the deviation from linearity in the Zimm plots using dilute aqueous PVA solutions, Matsuo and Inagaki[1] measured the weight-average molecular weight at a temperature of 80°C. The curvature of the Zimm plots at room temperature may be due to the fact that the PVA molecules are not isolated random coils but form superstructures with different sizes. This characteristic of PVA chains in solution is one of the most important problems in studying the drawability of dried PVA gel films[2,3]. The dynamics for the sol–gel transition of aqueous PVA solution have been investigated by Komatsu *et al.*, using the elastic light scattering technique[4]. They pointed out that this system has a phase diagram in which the spinodal curve crosses the sol–gel transition curve. According to their report, the spinodal points and sol–gel transition curves divided the phase diagram into four regions: (i) a homogeneous sol region; (ii) a sol region under the spinodal curve, indicating only spinodal decomposition; (iii) a gel region under the spinodal curve, indicating simultaneous advance of gelation and spinodal decomposition; and (iv) a gel region above the spinodal line, independent of liquid–liquid separation.

On the other hand, Fang and Brown have studied the time distribution of permanent PVA gels by the crosslinking of glutaraldehyde and corresponding semidilute solutions of polymer with narrow molecular-weight distribution[5]. They pointed out that there exist two relaxation modes for a PVA solution: fast relaxation characterizes the diffusive motion in the transient gel formed by interpenetration of molecular domains, while the slow mode is due to clusters and/or groups of chains having a size dependent on the concentration and only slightly on the temperature.

Except for the above reports[2–5], detailed analysis of the phase separation of PVA solutions has never been published. Thus this paper is concerned with the kinetics for the phase separation of aqueous PVA solution as a function of temperature and concentration in relation to the diffusive motion of PVA chains in solutions and gels by using elastic and inelastic light scattering.

EXPERIMENTAL

The sample used was atactic pellets with a 98% degree of hydrolysis. The degree of polymerization was 2000 estimated from the viscosity. The ratio M_w/M_n (M_w is the weight-average molecular weight and M_n is the number-average molecular weight) was estimated to be 3.20 by gel permeation chromatography. The solution in a transparent glass tube was prepared by heating a well blended polymer/solvent mixture at 105°C for 40 min in a di-n-butyl phthalate (DNBP) bath. Before putting the sample solution tube into the light scattering apparatus, which used a 632.8 nm He–Ne gas laser (DLS-700, produced by Ohtsuka Electrics Co. Ltd), the solution was pre-cooled by dipping it into a DNBP bath kept at 40°C

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*To whom correspondence should be addressed for 10 min. When the pre-cooled tube was put into a thermoregulated DNBP bath in the light scattering apparatus, it underwent a further drop to the desired temperature. The sample was pre-cooled to avoid convection in the fluid caused by an extremely rapid temperature drop. The change in angular distribution of the scattered light intensity with time was measured during the isothermal phase-separation process of the solution.

Photon correlation measurements were carried out by using the same light scattering apparatus (DLS-700), which was constructed in modules and has been discussed elsewhere[6,7].

To study the gelation mechanism at a macroscopic level, the solution in a test tube heated at 105°C for 40 min was quenched in a silicone oil bath at constant temperature. The test tube was closed with a cap to avoid any evaporation of the solvent during the measurements. After standing for 5 days in the bath kept at the same temperature, the test tube was tilted. When the meniscus deformed but the specimen did not flow under its own weight, we judged that the solution had gelled. We define the highest temperature for achieving gelation within 5 days to be the gelation temperature. This is in accordance with the method of Komatsu *et al.*[4].

The specific viscosity was measured by an Ubbelohde-type capillary viscometer after the polymer/solvent mixture had been set at the desired temperature for 15 min. The polymer/solvent mixture was well blended at 105°C for 40 min in the capillary viscometer and then cooled down to the desired temperature.

RESULTS AND DISCUSSION

Figure 1 shows the change in the logarithm of the scattered light intensity as a function of time for various values of q, observed for 10 g/100 ml aqueous PVA solutions, where the magnitude of the scattering vector is $q=(4\pi/\lambda)\sin(\theta/2)$, λ and θ being the wavelength of light in solution and the scattering angle, respectively. Except for the very short time over which convection occurs in the fluid, the logarithm of the scattered intensity increases linearly with time in the initial stage. The period of linearity becomes longer with increasing temperature but is much shorter than that for a dimethylsulfoxide/water mixture in the range 7–11°C. If these linear changes in the scattered intensity can be outwardly described by the linear theory of spinodal decomposition proposed by Cahn, we can obtain[7]:

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

where $I(q,t)$ is the scattered intensity at time t after initiation of the spinodal decomposition, and $R(q)$ is the growth rate of concentration fluctuation given as a function of q. The rate $R(q)$ is given by:

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

where D_c is the translational diffusion coefficient of the molecules in solution, f is the free energy of mixing, c is the concentration of the solution and κ is the concentration-gradient energy coefficient defined by Cahn and Hilliard[8]. A linear relationship for the plots of $\ln(I)$ vs. t at fixed q was also obtained for solutions with other concentrations at various temperatures. Following the linear theory, a plot of $\ln(I)$ vs. t at fixed q would yield a straight line of slope $2R(q)$, according to equation (1). With time, the logarithm of scattered intensity tends to deviate from the linear relationship, as has been observed in the later stage of spinodal decomposition[9]. This deviation shifted towards shorter time with decreasing temperature. This trend was more pronounced with increasing concentration of solution,

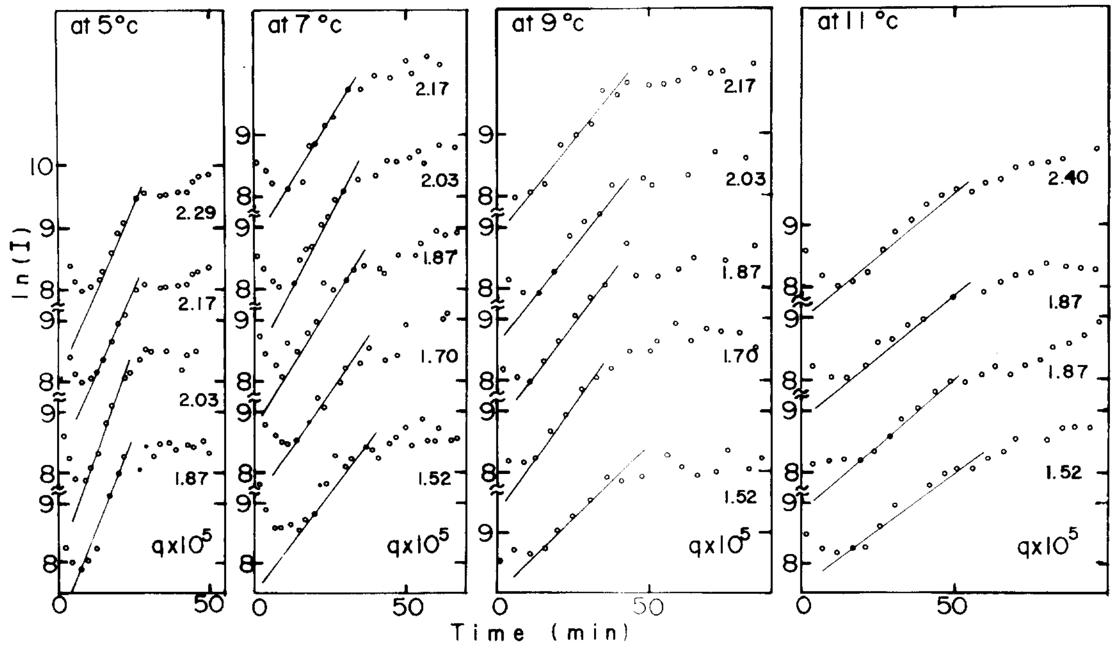

Figure 1 Change in the logarithm of scattered intensity against time for various values of q measured with 10 g/100 ml PVA solution at temperatures of 5, 7, 9 and 11°C

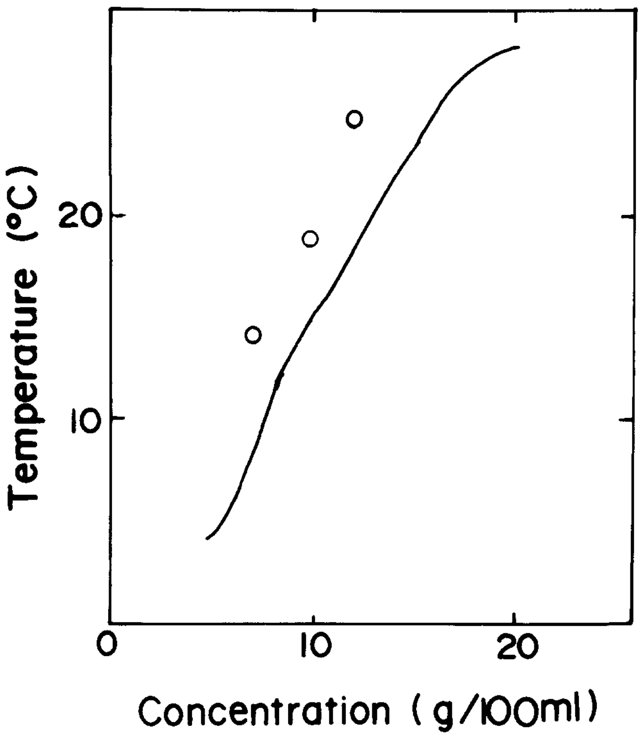

Figure 2 Spinodal and gelation temperatures vs. concentration. The full curve shows the gelation temperature vs. concentration and open circles represent spinodal temperature T_s vs. concentration

although the results for other concentrations are not shown in this paper.

Based on equation (2), a good linear relationship of a plot of $R(q)/q^2$ vs. q^2 was obtained experimentally, indicating that the initial stage of phase separation to form polymer-rich and polymer-poor phases can be described within the framework of the linear theory. The apparent diffusion coefficient $D_{app} = -D_c\ (\partial^2 f/\partial^2 c)$ is given by the intercept on the vertical axis. Furthermore, a plot of D_{app} vs. temperature also shows good linearity and, from the intercept on the temperature axis, one can estimate the spinodal temperature T_s at which D_{app} is zero. The values of T_s were 14.03, 18.60 and 25.04°C for the 7, 10 and 12 g/100 ml concentrations, respectively. This indicates that T_s becomes higher as concentration increases.

Figure 2 shows a plot of T_s vs. concentration (open circles), obtained on the basis of the assumption that the linear changes in the scattered intensity in *Figure 1* can be outwardly described by the linear theory of spinodal decomposition proposed by Cahn. The full curve shows the concentration dependence of the gelation temperature. At temperatures above the curve, it seems that the sol–gel transition cannot occur and there are two possibilities: one is a homogeneous sol region, while the other is a sol region under the spinodal temperature indicating the progress of spindal decomposition. This analysis, however, remains an unresolved problem. A definite scattering peak as a function of q, characterizing the later stage of spinodal decomposition reported for certain blend polymers[10], was not observed the sol region under the spinodal temperature. At temperatures below the curve, indicating simultaneous progess of gelation and spinodal decomposition, the advance of both mechanisms became faster as the temperature decreased. Namely, the gelation temperature is lower than T_s in the given concentration range. This behaviour is quite different from the results reported by Komatsu *et al.*[4]. It should be noted that the gelation of PVA solution is very sensitive to the type of solvent. That is, in spite of the same pellets, no gelation could be observed at 1 g/100 ml concentration for aqueous solutions, although progressive gelation for the dimethylsulfoxide/water mixture was confirmed at that concentration[3].

Figure 3 shows examples of the light scattering patterns under Hv polarization conditions, and logarithmic plots of the scattered intensity at $\theta = 90°$ as a function of time. These results were obtained for the 10 g/100 ml solution at 12°C. The observation was made at a temperature lower than T_s to check whether pure spinodal decomposition occurred at the initial stage, assuring the straight line of ln(I) vs. time, and gelation occurred at the later stage, showing the deviation from the straight line. In the given time, range no Hv light scattering patterns could be observed apart from incidental small spots, which were an artifact due to reflection of the incident beam. This indicates no existence of superstructure detected at the wavelength of the He–Ne gas laser beam. This is quite different from the phase separation of the PVA gels prepared from the dimethylsulfoxide/water mixtures with 70/30 and 50/50 compositions. According to previous work[3], the Hv scattering geometry showed an X-type pattern, indicating the existence of rod-like textures, the optical axes being oriented parallel or perpendicular to the rod axis[11], when the plots of ln(I) vs. time deviated from the straight line with increasing time. As discussed in the previous paper[3], we have proposed one possibility that, through the appearance of such an X-type pattern, the phase separation of PVA solution for dimethylsulfoxide/water mixtures did not reflect pure spinodal decomposition but indicated the possibility of simultaneous progress of gelation and spinodal decomposition. In contrast, the phase separation of the aqueous PVA solutions cannot be determined as the same mechanism directly because of the lack of Hv light scattering.

Figure 4 shows $R(q)$ plotted as a function of q for the 10 g/100 ml concentration. The maximum growth rate of concentration fluctuation $R(q)$ increases with decreasing temperature. The maximum relaxation rate $R(q_m)$

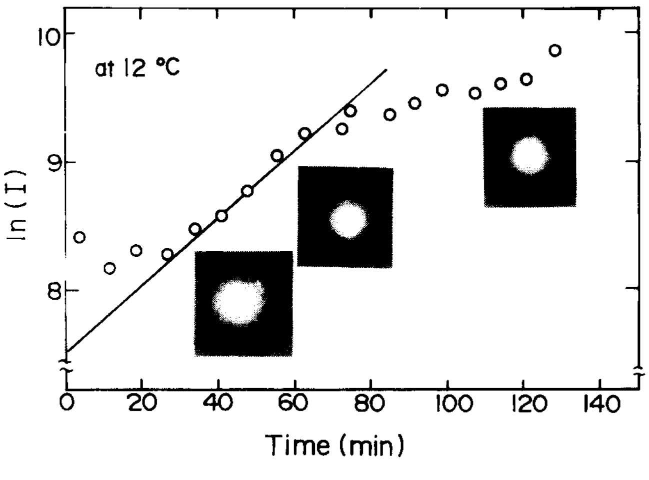

Figure 3 Change in ln(I) at $\theta = 90°$ and Hv light scattering patterns with time as measured for the 10 g/100 ml solution at 12°C

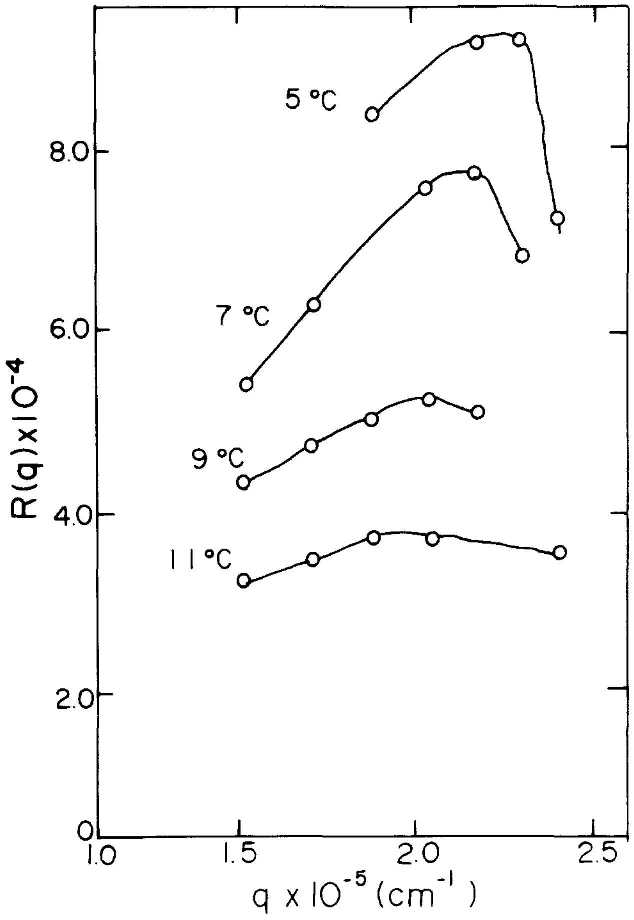

Figure 4 Variation in growth rate $R(q)$ of spinodal decomposition with q measured for the 10 g/100 ml solutions at the indicated temperatures

increases from 3.9×10^{-4} to 7.3×10^{-4} s^{-1} and the value of the scattering vector q_m shifts towards the scattering centre with decreasing difference $(T_s - T)$ between the measurable temperature T and spinodal temperature T_s ($=18.6$°C). According to van Aartsen's theory[12], the value of q_m increases with increasing difference $(T_s - T)$, if the range of molecular interaction associated with the mean-square radius of gyration based on the Debye concept is independent of temperature[13]. Hence, this behaviour apparently satisfies the principle of linearized spinodal decomposition for amorphous polymer solutions proposed by van Aartsen[12]. To check the temperature dependence of the mean-square radius of gyration, the plots of $R_H(q)$ vs. q^2 were done according to the Debye concept[13]. Unfortunately, the plots close to $q=0$ contain unfavourable factors such as multiple scattering. To avoid multiple scattering, the correlation distance is estimated at several temperatures according to Debye–Bueche theory[14]. That is:

$$R_H(q)=\langle\eta^2\rangle\int_0^{\infty}\gamma(r)\frac{\sin(qr)}{qr}r^2\,\mathrm{d}r \qquad (3)$$

where $R_H(q)$ is the Rayleigh ratio given as a function of the magnitude of the scattering vector q, $\langle\eta^2\rangle$ is the mean-square fluctuation in average polarizability and $\gamma(r)$ is a correlation function. If $\gamma(r)$ is given by $\exp(-r/a)$, equation (3) reduces to:

$$R_H(q)^{-1/2}=(8\pi\langle\eta^2\rangle a^3)^{-1/2}\,(1+a^2q^2) \qquad (4)$$

For several experimental results, *Figure 5* shows examples of the relationship between $R_H(q)^{-1/2}$ and q^2 at 1 g/100 ml concentration. The reciprocal root plots of $R_H(q)$ in equation (4) can restrict the multiple scattering effect at smaller angle, apparently, in comparison with the plots of $R_H(q)$ vs. q^2 associated with the equation to obtain the mean radius of gyration by Debye[13]. Most of the plots show a fairly linear relationship except at very small values of q^2, regardless of temperature. The correlation distance a obtained from the slope of the linear plots of $R_H(q)^{-1/2}$ vs. q^2 is listed in *Table 1*. The values increase slightly with temperature and concentration in the given range. Here it should be noted that the physical meaning of the correlation distance is related to the concentration of solution[15,16]. If the solution is dilute, a is related to the domain size, which allows the assumption that the correlation distance is proportional to the mean radius of gyration. In contrast, if the given concentration is high, a is not simply related to the size of the structural unit but depends upon both interparticle and intraparticle distance. Judging from the results in *Table 1*, it may be concluded that, if the correlation

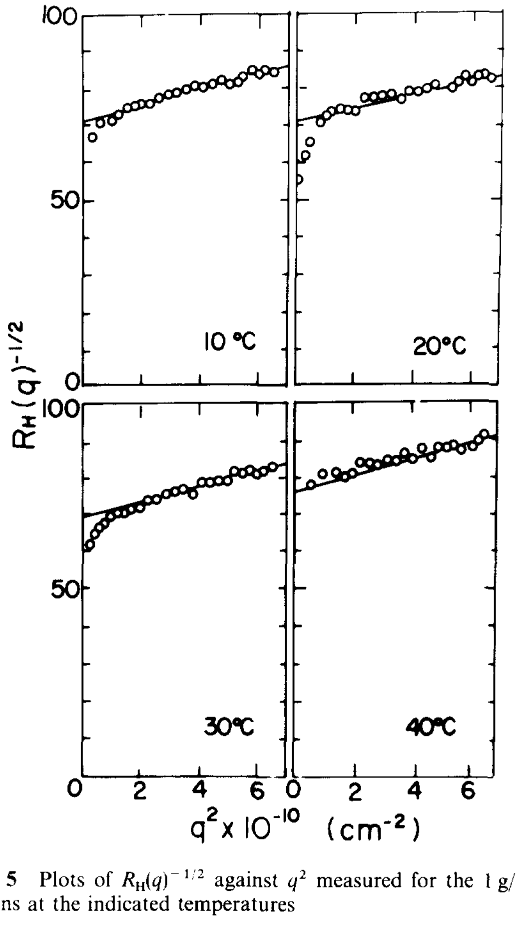

Figure 5 Plots of $R_H(q)^{-1/2}$ against q^2 measured for the 1 g/100 ml solutions at the indicated temperatures

Table 1 Temperature dependence of correlation distance (nm) in the 0.001 and 1 g/100 ml concentrations

Concentration (g/100 ml)	Temperature (°C)			
	10	20	30	40
0.001	13.3	14.3	15.6	15.9
1.0	13.3	15.0	16.0	17.1

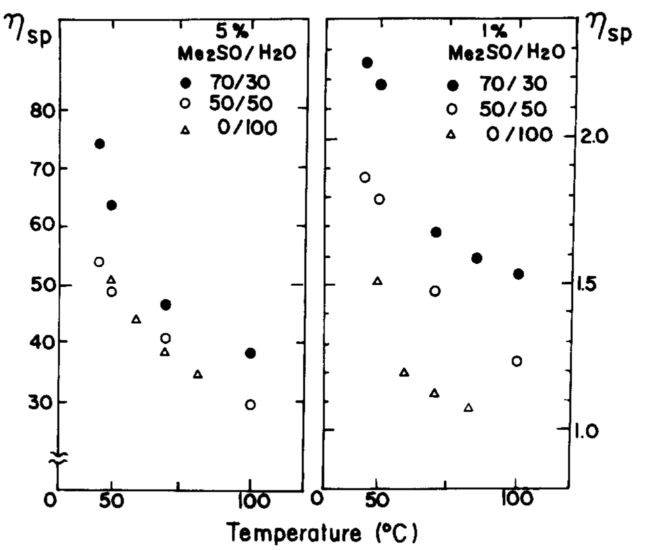

Figure 6 Specific viscosity η_{sp} against temperature measured for the 5 and 1 g/100 ml solutions. For abbreviation, the unit of g/100 ml is termed % in this figure

distance is related to the domain size, the size of the domains becomes slightly bigger with increasing temperature but is almost constant around 10°C. The values are in the range 13.3–17.1 nm and these values are lower than the values (50–75 nm) obtained in dimethylsulfoxide/water mixtures with 0.1 and 2 g/100 ml concentrations[3]. This trend reflects the lower values of specific viscosity plotted against temperature as shown in *Figure 6*, and this tendency becomes considerable with decreasing concentration. This implies that water is a poorer solvent for PA molecules than dimethylsulfoxide/water mixtures.

Returning to *Figure 4*, it may be expected that the plots of $R(q)$ vs. q in the temperature range 5–11°C indicate spinodal decomposition, since the correlation distance listed in *Table 1* is almost unchanged. To satisfy this concept, however, the translational diffusion coefficient of the molecules in solution must be constant regardless of time. To check this, inelastic light scattering measurements were carried out for aqueous PVA solutions. The evaluation of the data was done by the cumulative method for determining the distribution of decay rate Γ from the observed autocorrelation function. Sample preparation was done according to the same method as the measurements in *Figure 1*. To estimate the diffusion coefficient, it is important to check that the plot yielded a linear relationship, thus assuring the definition of D by $\Gamma = Dq^2$. In the timescale <3 h, however, the phase separation was too rapid to measure Γ at various values of θ by assuming that the equilibrium state of PVA solution was maintained during the Γ measurement at various θ values. This means that it is difficult to check the linearity of Γ against q^2 in the timescale <3 h. Thus, the time dependence of Γ/q^2 was estimated only at $\theta = 90°$ using a cumulative method.

The measurements were done for the solution with the 5 g/100 ml concentration. *Figure 7a* shows the time dependence of Γ/q^2 at $\theta = 90°$ and *Figure 7b* corresponds to the time dependence of $\ln(I)$. The autocorrelation function was measured for the photon counting period of 5 min, by assuming that the equilibrium state in solution is maintained during that period. It is seen that, even in the time range showing the straight line of $\ln(I)$ vs. time, the value of Γ/q^2 decreased rapidly, and when $\ln(I)$ deviated from the linear relationship, the value of Γ/q^2 tended to level off. Judging from this behaviour, it may be concluded that the linear relationship of $\ln(I)$ vs. time does not reflect the initial stage of pure spinodal decomposition associated with the linear theory proposed by Cahn[7], but indicates the simultaneous progess of gelation and spinodal decomposition. Of course, the deviation from the straight line in the $\ln(I)$ vs. time plot is essentially different from the later stage of phase separation reported for polymer blends[7]. That is, in a polymer blend system, further growth in concentration fluctuation associated with upward diffusion is significant in the later stage of spinodal decomposition, and the concentration profile finally becomes similar to that of nuclear growth. In the present PVA solutions, however, such further growth in concentration fluctuation was suppressed because of immobilization of the PVA chains due to crystallization. That is, a very weak broadly overlapped X-ray diffraction intensity distribution from the (1 0 1) and (1 0 1) planes was observed by X-ray diffraction. This phenomenon was also confirmed for the gels prepared from the dimethylsulfoxide/water mixtures[3].

Here it should be noted that, in spite of the same measurable ratio between D associated with a typical simple system satisfying Fick's second law by inelastic light scattering and D_c associated with spinodal decomposition by elastic light scattering, the time dependence of Γ contradicts the linear relationship of

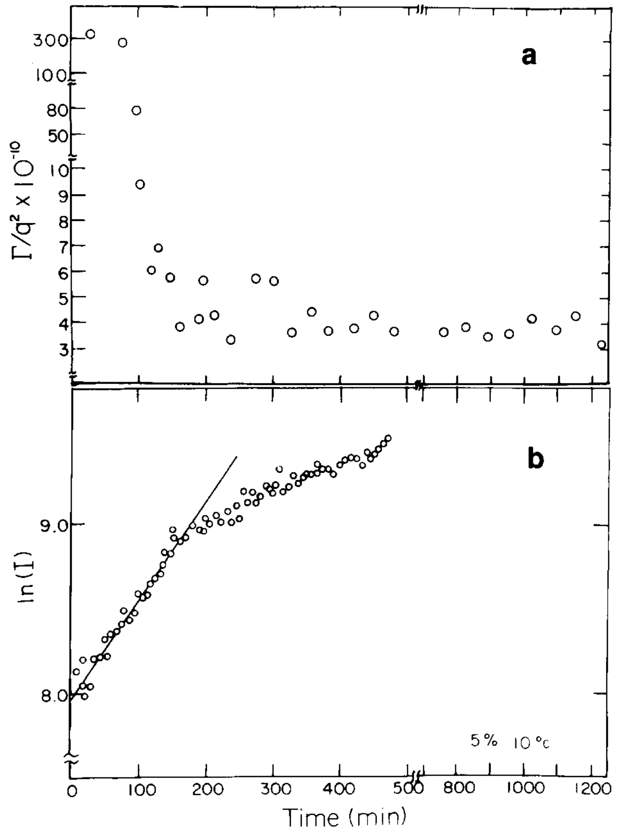

Figure 7 (a) The time dependence of Γ/q^2 for 5 g/100 ml solutions at 10°C and (b) the change in $\ln(I)$ at $\theta = 90°$

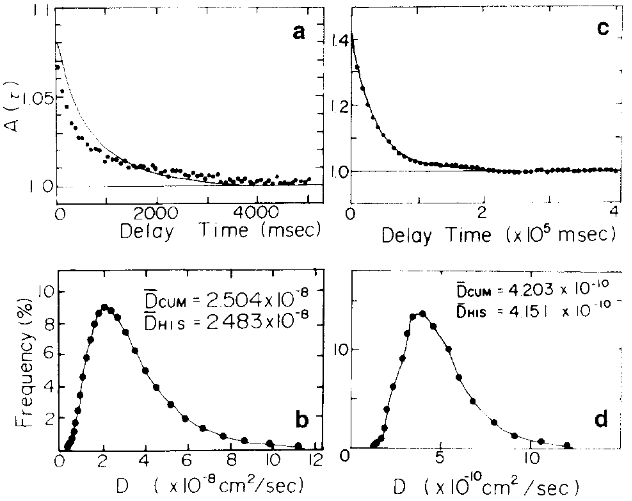

Figure 8 (a) Autocorrelation function $A(\tau)$ against decay time at 10°C for the 1 g/100 ml concentration and (b) the corresponding distribution function of diffusion coefficient D calculated by the histogram method. (c) Autocorrelation function $A(\tau)$ against decay time at 10°C for the 5 g/100 ml concentration and (d) the corresponding distribution function of diffusion coefficient D. The curves in (b) and (d) were drawn to follow the points calculated for the gravity of the distribution of the diffusion coefficient

ln(I) vs. time, if the linear relationship can be described by the linear theory of spinodal decomposition proposed by Cahn[7]. Judging from the results in *Figure 7*, equation (1) must be essentially given by:

$$I(q,t) = I(q,t=0)\ \exp[Q(q,t)] \qquad (5)$$

In this case, even if $Q(q,t)$ is represented as a complicated function of t, it must be described as $2R(q)t$, approximately, to satisfy the linear relationship of ln(I) vs. t in *Figure 1*. However, two problems can arise: one is whether phase separation of the aqueous solution of PVA as well as dimethylsulfoxide/water mixtures is really dependent upon spinidal decomposition by Cahn's theory in spite of the linear relationship; the other is due to the inevitable measurement of the autocorrelation function obtained by assuming that the equilibrium state in solution is maintained during the photon counting period of 5 min. Even so, we must remember the uncertainty that the phase separation of aqueous PVA solution in the initial stage in the linear part of ln(I) vs. t is attributed to spinodal decomposition. Unfortunately, this problem still remains unresolved. Accordingly, it may be taken into consideration that, as one of the possibilities, the phase separation of PVA solution consists of the simultaneous progress of spinodal decomposition and gelation.

Finally, the diffusion coefficients are estimated by the histogram method, based on an autocorrelation function $A(\tau)$ plotted against decay time τ for the 1 mg/100 ml and 5 g/100 ml solutions at 10°C, respectively, in order to study the molecular mobility during the later stage of phase separation associated with the gelation. The measurements were done after 1 day when th pre-cooled tube had been put into a thermoregulated DNBP bath in the light scattering apparatus, in order to allow measurements of the q^2 dependence of the change in Γ. From the time independence of Γ/q^2 of the storage specimens, it was confirmed that the mobility of PVA chains in solution assures the equilibrium state. Of course, before these measurements, the q^2 dependence of Γ calculated by the cumulative method was confirmed to exhibit a linear relationship. *Figure 8a* shows the autocorrelation function $A(\tau)$ plotted against decay time τ and *Figure 8b* shows the distribution of the diffusion coefficient D calcuated by the histogram method for the 1 mg/100 ml solution at 10°C. *Figures 8c* and *8d* show the autocorrelation function and the distribution of D for the 5 g/100 ml solution, respectively. The points in (a) and (c) are the experimental results and the curves were recalculated from the histogram obtained by assuming a unimodal system.

As shown in *Figure 8b*, the mean value (D_{HIS}) estimated as the centre of gravity of the distribution curve and the value of D_{CUM} calculated by the cumulative method are listed together. It is seen that, in spite of smaller values of $A(\tau)$ around $\tau = 0$, the values of D_{HIS} are in good agreement with that of D_{CUM}, indicating reliability of the distribution of D. The values of D_{HIS} and D_{CUM} for the aqueous solutions with the 1 g/100 ml concentration at 10°C are larger than those for dimethylsulfoxide/water mixtures with the same concentration at 20°C[3], indicating active diffusive motion of PVA molecules in solvents and gels. This phenomenon supports the idea that the active molecular mobility in solvents and gels tends to prevent rapid gelation, since the gelation temperature, 5°C, of the aqueous solution with 5 g/100 ml concentration is lower than that, 30°C, of the dimethylsulfoxide/water mixtures with the same concentration[3]. Accordingly, it turns out that the diffusion coefficient of PVA molecules in solvent associated with gelation is strongly affected by the kinds of solvents in addition to concentrations.

CONCLUSION

Phase separation of aqueous PVA solution was studied by elastic and inelastic light scattering. The logarithm of scattered intensity against time yielded a straight line in the initial stage of phase separation, and started to deviate from this linearity in the latter stage. In the phase-separation process, no scattering pattern could be observed under Hv polarization conditions. The correlation distance was slightly longer with increasing concentration and temperature in the range of 0.001–1 g/100 ml. The value of Γ/q^2 decreased markedly in the sol region at less than the spinodal temperature. If the linear relationship can be described within the framework of the linear theory by Cahn[7], Γ/q^2 must be a constant value regardless of time, indicating the progress of phase separation by spinodal decomposition only. Such a contradiction of the phase diagram shown in *Figure 2* is due to the criterion defined for gelation: the meniscus deformed but the specimen did not flow under its own weight when the solution in a test tube was tilted. This indicates that, even in the region observed as a sol at the macroscopic level, gelation occurred locally within the sol region.

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