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Molecular aggregation behavior of polyvinyl chloride solutions

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Abstract

In this work, the effects of the polymer–solvent interaction on the aggregation behavior of polyvinyl chloride (PVC) solutions were studied through elastic light scattering and viscosity measurements. The result in Zimm plots of PVC solutions showed that the second viral coefficient, A_2, value of PVC/BrBz solutions is higher than that of PVC/DOA solutions at the same temperature. The radius of gyration, R_g, in PVC/BrBz solutions is larger than that in PVC/DOA solutions, indicating that PVC chains in a good solvent BrBz must be more extended than those in a poor solvent, DOA. The θ-temperatures are about 32°C and 68°C for PVC/BrBz and PVC/DOA solutions, respectively. The result in the temperature dependence of R_g value showed that PVC/BrBz solution exhibits the coil–globule transition, while no transition is observed in PVC/DOA solution in the measured temperature range. The chain overlapping concept was used to discuss the heterogeneous degree of PVC solution. The result showed that PVC/DOA solution is more heterogeneous than PVC/BrBz solution. The time-resolved light scattering measurements indicated that the spinodal decomposition rate of PVC/DOA solution was faster than that of PVC/BrBz solution. However, the gelation time of PVC/BrBz solution was shorter than that of PVC/DOA solution. These facts may imply that the more extended chains in PVC/BrBz solution are advantageous to the intermolecular association for the gelation. The scattered profiles ($I(q)$ vs. q) showed that the scattered intensity of PVC/DOA solution is much higher than that of PVC/BrBz solution at the same concentration. A scattered maximum was observed in PVC/DOA solution while no other peak appeared in PVC/BrBz solution. The various aggregation or the gelation behaviors between PVC/DOA and PVC/BrBz solutions must be concerned with different degrees of spinodal decomposition in the solution state, which is mainly related to different degrees of the polymer–solvent interaction.

Keywords: Polyvinyl chloride; Elastic light scattering; Spinodal decomposition

1. Introduction

It is well known that polyvinyl chloride (PVC) is a polar and low crystalline polymer, which can form physical polymer gels in a variety of solvents with the formation of fringed micelle microcrystals as junction points in the network structure [1–10]. Generally, the molecular aggregation and the gelation behaviors in polymer solutions are affected by many factors, such as the temperature, the molecular weight and the concentration of the polymer, the species of the solvents used and so on. How the solvent quality affects the gelation mechanism is still a question unresolved. Recently, in our previous studies [1,2], we reported that the physical properties of PVC gels were functions of the molecular volume of solvent, V_S, and the polymer–solvent interaction. The results showed that physical properties such as the modulus and melting point of gels are strongly dependent on the aggregation degree of polymer chains related to the solvent type used. On the other hand, also in our previous studies [11,12], polyvinyl alcohol (PVA) gels prepared from both ethylene glycol (EG) and N-methyl-2-pyrrolidone (NMP) solutions showed that the melting temperature and crystallinity of PVA/EG gels were higher than those of PVA/NMP gels. It should be noted that the solubility of PVA in NMP is higher than that in EG. These results let us consider that the polymer–solvent interaction must play an important role on the aggregation behavior for polymer chains during the gelation of the solution. The polymer chains in solution exhibit different conformations, which are mainly dependent on the polymer–solvent interaction. In a good solvent, the polymer chain exhibits a more extended coil, while in a poor solvent, the polymer chain is collapsed and then intramolecular aggregation occurs easily. The molecular structure of PVC thermoreversible gels has been studied by Dahmani et al. [13] with light scattering, and by Reincke et al. [14] with neutron scattering. Dahmani et al. reported that the fiber rigidity in the gel network is independent of the solvent type used. On the other hand, Reincke et al. pointed out that the structure and physical properties of PVC gels

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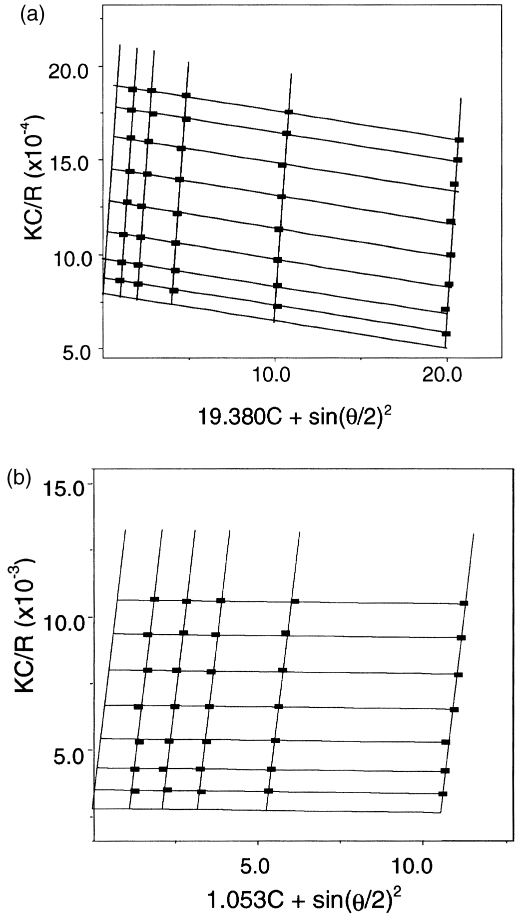

Fig. 1. Zimm plots of PVC dilute solutions at 30°C: (a) PVC/DOA solution; (b) PVC/BrBz solution.

formed with organic solvents such as diesters and bromobenzene were strongly related to the polymer–solvent interaction.

Recently, several studies on the kinetics of spinodal decomposition in polymer gels and in polymer solutions have been published [15–20]. Bansil et al. [15,16] studied the effects of spinodal decomposition kinetics on the gelation mechanism of gelatin. Their results indicated clearly that the occurrence of gelation has a pronounced effect on the dynamics of phase separation and on the scaling laws describing the time evolution of domain growth. Matsuo et al. [18,19] have also studied the phase separation behavior of PVA in DMSO/H_2O mixed solutions through elastic light scattering technique and showed that the logarithm of scattered intensity from the PVA solution increased linearly with time at the initial stage of phase separation. On the other hand, Otake et al. [20] reported that the early stage for spinodal decomposition of the gel volume phase transition is similar to that of a typical polymer solution and can be understood based on the Cahn–Hilliard–Cook (CHC) theory [21,22] through the studies of the time-resolved light scattering. The spinodal decomposition of polymer solution must be concerned with the polymer–solvent interaction, when a solution undergoes phase separation from a one-phase state to a two-phase coexistence state during the gelation.

In this work, we first study the molecular interaction between PVC and organic solvents such as bromobenzene ($\delta = 9.9$, $V_S = 104.75\ \mathrm{cm^3\ mole^{-1}}$) and dioxane ($\delta = 10.0$, $V_S = 85.21\ \mathrm{cm^3\ mole^{-1}}$) solvents which have a similar solubility parameter, δ, but a different molar volume. Then, the relationship between the polymer–solvent interaction and the molecular aggregation or the gelation behaviors of PVC solutions was discussed.

2. Experimental

2.1. Sample preparation

PVC used in this work was laboratory grade powder with the weight-average molecular weight, $M_w = 50.0 \times 10^4\ \mathrm{g\ mole^{-1}}$ ($M_w/M_n = 5.32$, Aldrich Chemical, USA). The solvents, bromobenzene (BrBz) and dioxane (DOA), were analytical grade and purified by distillation and filtered by using 0.045 μm Millipore filters for removing dust before using. The PVC solutions were prepared in a precleaned wide mouth bottle with stirring at 95°C for 2 h until dissolved into a homogeneous solution. The stock solutions were filtered through a 0.22 μm Millipore filter into optical cells and diluted with dust-free solvent to obtain the desired concentration. Subsequently, the optical cells were kept in a thermostat oven at a constant temperature of 30°C for at least 1 week to stabilize the solutions before light scattering measurements.

2.2. Measurements

Light scattering measurements were carried out by using a Malvern series 4700 apparatus with an Ar ion laser (LiCONiX 5100) operating at a wavelength of 514.5 nm as light source. The Optilab DSP interferometic refractometer was operated at the same condition of light scattering measurement for obtaining the refractive index increment values, *dn*/*dc*, for PVC solutions. The *dn*/*dc* values for PVC/DOA and PVC/BrBz solution are 0.097 and 0.013 ml g^{-1} at 30°C, respectively. The reduced scattering intensity, KC/R_θ, was derived, where C is the concentration and R_θ is the Rayleigh ratio obtained through the calibration using toluene; $R_{90} = 18 \times 10^{-6}\ \mathrm{cm^{-1}}$. This value was used for the calculation of the Rayleigh ratio of PVC solutions. The time dependence of scattering intensity during the isothermal phase separation was measured using the step scattering measurement in the scattering vector (q) range of $4.06\ \mu\mathrm{m}^{-1} \le q \le 15.16\ \mu\mathrm{m}^{-1}$ [$q = (4n\pi/\lambda)\sin(\theta/2)$, where θ is the scattering angle, and n is the refractive index of the medium].

The viscosity of PVC solution was measured using a CJV1000 vibro viscometer [23] (Tohoku Densi, Japan). PVC solutions were heated at 95 ~ 110°C until they dissolved into homogeneous solution; then the solutions were quickly cooled to 30°C for 2 h.

The gelation time was measured using a gelation timer (Techne, UK) operating at a fixed temperature of 30°C. The determination of gelation time was carried out using a flat weighted disc connected by a link with a synchronous motor falling under gravity in the polymer solution. At the gelation point the rigidity of the polymer is sufficient to support the weight of the disc and causes the link to be compressed and to stop the synchronous motor. The time at which the synchronous motor stopped was defined as the gelation time.

3. Results and discussion

Fig. 1(a,b) shows the Zimm plots of light scattering for PVC/DOA and PVC/BrBz dilute solutions with $M_w = 50 \times 10^4$ g mol^{-1} at 30°C, respectively. The values of the second viral coefficient, A_2, and the radius of gyration, R_g, were directly obtained from the Zimm plots in Fig. 1 through the following equation [24,25]:

$$\frac{KC}{R_\theta} = \frac{1}{\bar{M}_w}\left[1 + \frac{16}{3}\pi^2\frac{\langle Rg^2\rangle}{\lambda_0^2}\sin^2\theta + \cdots\right] + 2A_2C + \cdots \tag{1}$$

The optical constant for vertically polarized light is $K = 4\pi^2 n_0^2(dn/dc)^2/N_A\lambda^4$ where n_0 is the solvent refractive index, dn/dc is the measured refractive index increment for PVC solution, λ_0 is the wavelength of light in a vacuum, N_A is Avogadro's number, R_θ is the Rayleigh ratio for the solution, θ denotes the scattering angle and C is the polymer concentration. The calculated result shows that PVC/DOA solution has a negative A_2 value (-1.18×10^{-3} cm^3 mol g^{-2}), indicating that a repulsive phenomenon appears between PVC chains and DOA at 30°C. On the other hand, PVC/BrBz solution shows a near zero A_2 value at 30°C, i.e. the repulsive force balances the attractive force between PVC chains and solvent for the PVC/BrBz solution at ca. 30°C. In other words, PVC chains in dilute BrBz solution yield an unperturbed state at this temperature. These results show clearly that the A_2 value of PVC/BrBz solution is higher than that of PVC/DOA solution at the same temperature. PVC chains in a good solvent, BrBz, must be more extended than those in a poor solvent, DOA. Recently, Mutin and Guenet [7] reported that Zimm plots of PVC solutions in both ethyl heptanoate and diethyl malonate exhibit a hook-shaped Zimm plot. They suggested that the aggregation of PVC chain in those solvents results in the formation of two types of scattering characteristics (block copolymers and intraparticular correlation). However, no hook-shaped Zimm plots of diluted PVC solutions were observed in this work, that is, PVC chains are isolated random coils without other superstructures. Besides, the R_g value in PVC/BrBz solution (ca. 104 nm) is also larger than that in PVC/DOA solution (ca. 71 nm) at 30°C, indicating that PVC has a much extended chain dimension in BrBz.

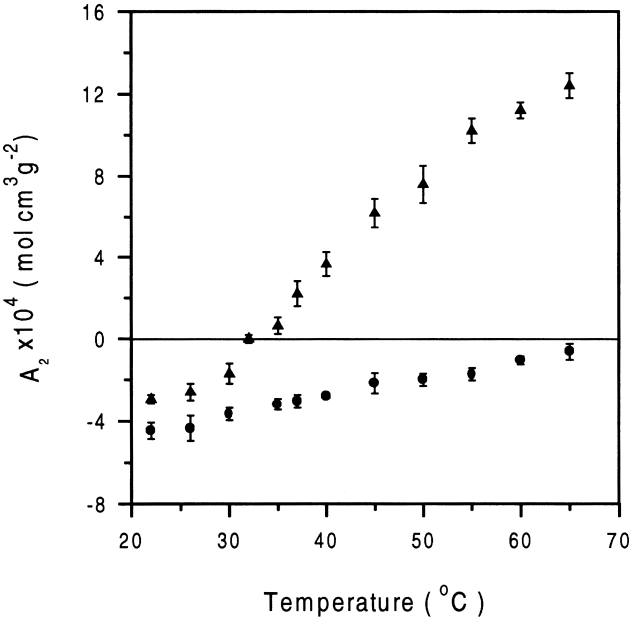

Fig. 2. Plots of the second viral coefficient, A_2, as a function of temperature for various PVC solutions at 30°C: (●) PVC/DOA solution; (▲) PVC/BrBz solution.

In order to obtain more information about the interaction between PVC and solvents, the temperature dependence of the Zimm plots was measured from 22°C to 65°C. Fig. 2 and Fig. 3 are the A_2 and the R_g values as a function of temperature for various PVC solutions, respectively. Fig. 2 shows that the A_2 value increases with increasing temperature, indicating that the solubility of PVC in the solvents increases with increasing temperature. The A_2 value of PVC solutions in both BrBz and DOA exhibits a negative A_2 value that increases with increasing temperature. Subsequently, the repulsive interaction force balances the attractive force between PVC chains and solvent at the temperature (θ-temperature) where the A_2 value becomes zero. The θ-temperatures obtained from the slope extrapolated to $A_2 = 0$ in Fig. 2 are about 32 and 68°C for PVC/BrBz and PVC/DOA solutions, respectively. On the other hand, the R_g value also increases as the temperature increases.

Polymer chains in a poor solvent must easily collapse and then aggregate, while polymer chains in a good solvent must be favorable to exhibit extended coil conformation. At the temperature below the θ-temperature, R_g becomes much smaller than the ideal radius of gyration, R_g^θ. Near the θ-temperature, only a small change in temperature causes a dramatic change in the R_g value; this change is called the coil–globule transition as shown in Fig. 3 for PVC/BrBz solution. The transition between the coil and the globule states has been widely discussed in many studies [26–29]. Sun et al. [26] reported that the temperature dependence of the R_g value for polystyrene in cyclohexane from good

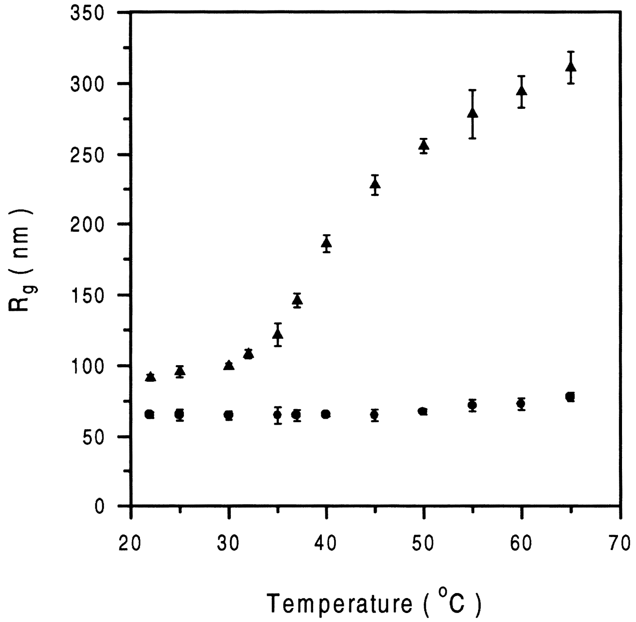

Fig. 3. Plots of the radius of gyration, R_g, as a function of temperature for various PVC solutions at 30°C: (●) PVC/DOA solution; (▲) PVC/BrBz solution.

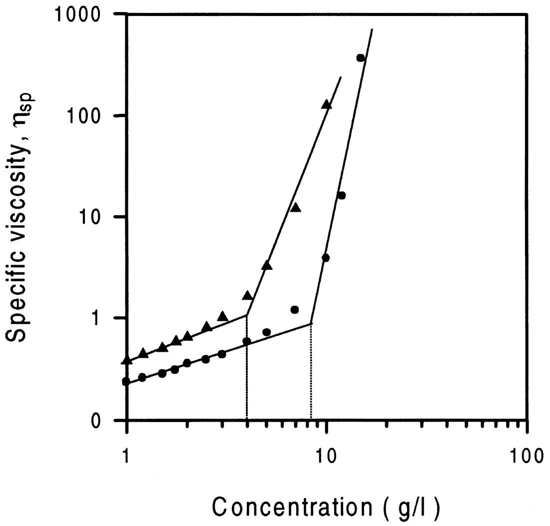

Fig. 4. Plots of $\ln\eta_{sp}$ versus concentration for various PVC solutions at 30°C: (●) PVC/DOA solution; (▲) PVC/BrBz solution.

solvent through poor solvent exhibited a coil–globule transition. They also pointed out that the coil–globule transition of polyacrylamide chain was induced by the solvent composition [27]. This means that the polymer–solvent interaction plays an important role on this transition. In Fig. 3, PVC/BrBz solution exhibits the coil–globule transition, while no transition is observed in PVC/DOA solution in the measured temperature range. This is because of the much higher θ-temperature of PVC/DOA (ca. 68°C) solution. It is reasonable that the chain dimension of PVC in poor solvent is comparatively difficult to change because of the low solubility. On the other hand, the R_g^θ value was obtained from Fig. 3 at θ-temperature. The R_g^θ values of PVC are about 106 and 78 nm for PVC/BrBz and PVC/DOA solutions, respectively. It is well known that the chain dimension of PVC unperturbed chains should be the same at the θ-condition. Therefore, the use of the same PVC must exhibit the same R_g^θ value, which is not affected by the species of the solvents used. The only difference between PVC/DOA and PCV/BrBz solutions under the θ-condition is the molar volume, V_S, of the solvent, that is, the V_S value of BrBz ($104.75\ \mathrm{cm^3\ mole^{-1}}$) is larger than that of DOA ($85.21\ \mathrm{cm^3\ mole^{-1}}$). It is still difficult to understand why the use of the solvent with larger V_S should have a higher R_g^θ value. However, the Flory–Huggins relation [30,31] indicates clearly that the V_S value is also an important factor on the melting point depression of polymer. In the other words, the gel prepared from the solvent with larger V_S showed a higher melting point at the same value of the interaction parameter, χ_1^1. The effects of V_S on the R_g^θ value and the melting temperature of gels are difficult to connect. The change of the R_g^θ value with the species of solvents is still an unresolved problem. Regardless of the R_g^θ result as mentioned above, the effects of the polymer–solvent interaction on the properties of PVC solutions such as viscosity and gelation time were discussed as follows.

Fig. 4 shows the $\log\eta_{sp}$ versus C plots of various PVC solutions, in which $\eta_{sp} = \eta/\eta_0 - 1$ using η and η_0 corresponding to the viscosities of solution and solvent, respectively. The viscosity result shows that as the polymer concentration is increased, the polymer chains start to overlap and begin to be entangled with each other, resulting in rapid increase of the viscosity. This indicates that there exists a critical gelation concentration, C^*, which can classify the specific viscosity approximately into two regions. When the polymer concentration of the solution is higher than C^*, infinite junction points are formed over the whole solution; polymer chains should be overlapped or entangled, while the polymer concentration of the solution is lower than C^*, which exhibits homogenous polymer solutions and cannot form gels. The polymer chains are necessarily overlapped for gelation from the solution. The two straight lines in Fig. 4 were drawn by a least squares method. The C^* values (intersection of the two lines) obtained from Fig. 4 are about 4.0 and $8.1\ \mathrm{g\ l^{-1}}$ for PVC/BrBz and PVC/DOA solutions, respectively. The C^* value of PVC/BrBz solution is smaller than that of PVC/DOA solution. This fact may be due to a larger R_g value making the chains more extended to increase the opportunity of the intermolecular association for the gelation at a given gelation temperature. The chain aggregation behavior between PVC/BrBz and PVC/DOA solutions must be very different due to the properties of the dilute solution state. Therefore, the chain overlap in these two solutions is further compared as follows. The overlapping concentration, $C_{Rg}{}^*$, for polymer chains from

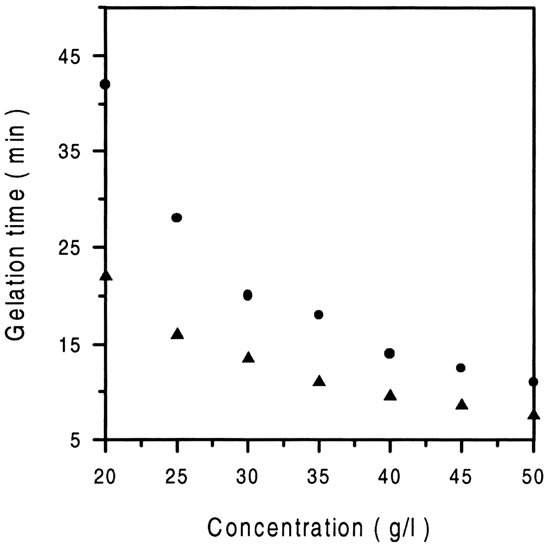

Fig. 5. Plots of gelation time versus concentration for various PVC solutions at 30°C: (●) PVC/DOA solution; (▲) PVC/BrBz solution.

the radius of gyration, R_g, is well known as given by:

$$C^*_{\mathrm{Rg}} \approx \frac{3M}{4\pi N_A R_g^3} \tag{2}$$

where M is the weight-average molecular weight, N_A is the Avogadro's number, and R_g values of PVC/BrBz and PVC/DOA solutions obtained from Fig. 3 are 104 and 71 nm at 30°C, respectively. The $C_{\mathrm{Rg}}*$ values are about 0.187 and 0.554 g l^{-1} for PVC/BrBz and PVC/DOA solutions, respectively.

Combination of the results as mentioned above shows that the $C*$ values are obviously different from the $C_{\mathrm{Rg}}*$ values in both PVC/BrBz and PVA/DOA solutions. Generally, it is natural to consider the chian overlapping concentration as the critical gelation concentration. This concept has been applied to the gelation of atactic polystyrene in carbon disulphide, indicating that the junction points in gel network were considered to be a complex between at-PS and CS_2 [32,33]. When the $C*$ value is in agreement with the $C_{\mathrm{Rg}}*$ value, the gelation occurs in a comparatively homogeneous solution without a large degree of liquid–liquid phase separation or spinodal decomposition. Ohkura et al. [34] have also discussed in detail about the chain overlapping concept for the gelation of polyvinyl alcohol/dimethyl sulphoxide/water solutions. Their results in PVA/DMSO/H_2O systems showed that the agreement between $C*$ and $C_{\mathrm{Rg}}*$ values is very good except for the sample which has the lowest molecular weight. However, Domszy et al. [35] pointed out that the chain overlapping concept was invalid in the gelation of linear polyethylenes in toluene or p-xylene, because the large size of the crystallite was formed as the junction point in the gel network. On the other hand, Papanagopoulos and Dondos [36] pointed out that the polymer chains during their motion showed a lower hydrodynamic volume, due to peripheral intermolecular entanglements and decreases in their volume because of collisions. Therefore, the critical concentration obtained by viscometer, $C*$, is larger than that obtained by static light scattering, $C_{\mathrm{Rg}}*$. With these backgrounds, it is naturally considered that the degree of the difference between $C*$ and $C_{\mathrm{Rg}}*$ values ($\Delta C*$) could be regarded as the heterogeneous degree of the solution system. In other words, the larger $\Delta C*$ ($\Delta C* = C* - C_{\mathrm{Rg}}*$) value of the solution should exhibit a larger degree of liquid–liquid phase separation or spinodal decomposition. Regarding the results in this work, the $\Delta C*$ value was found in both PVC/BrBz and PVC/DOA solutions. The chain overlapping concept cannot be suitable to this study because the gelation or the molecular aggregation behaviors may be caused by the phase separation from heterogeneous solution. The $\Delta C*$ value in PVC/DOA solution (7.55 g l^{-1}) is higher than that in PVC/BrBz solution (3.91 g l^{-1}), indicating that PVA/DOA solution must exhibit a larger degree of liquid–liquid phase separation or spinodal decomposition than PVC/BrBz solution does. The poor solubility of the solvent used should be more favorable to intramolecular aggregation of PVC chains, resulting in a comparatively heterogeneous solution.

Fig. 5 shows the gelation time as a function of polymer concentration at 30°C. The gelation time of PVC/BrBz solutions is shorter than that of PVC/DOA solutions at all measuring concentrations. This result is very interesting in that the gelation rate of the solution with good solvent is faster than that of the solution with poor solvent. Matsuo et al. [37] reported that the size or spatial extension of the polymer chains in solution has a significant effect on the spinodal decomposition and gelation, and that the intramolecular coupling entanglements play a more important role in promoting spinodal decomposition and gelation rather than the intermolecular decomposition. On the other hand, Komatsu et al. [38] reported that the spinodal and the sol–gel transition curves for PVA solutions cold divide the phase diagram into four regions: (1) a homogeneous sol region, (2) a sol region under the spinodal curve, (3) a gel region under spinodal curve, and (4) a gel region above the spinodal curve. They considered that the supermolecular structure in the PVA system developed in region (3) where the PVA solution must be influenced by liquid–liquid phase separation in the early stage of gelation. From the above discussion, however, the spinodal decomposition behavior of the PVC solution might be quite different from phase separation of the PVA solution because the crystallization ability of atactic PVC is much lower than that of atactic PVA. The different gelation time of PVC solutions is considered due to the different aggregation behavior of PVC chains in various solutions. In PVC/BrBz solutions, the larger value of R_g related to the higher polymer–solvent interaction must make PVC chains become more extended to increase the opportunity for the intermolecular association. On the other hand, the smaller R_g value in PVC/DOA solution may make the intramolecular association of PVC

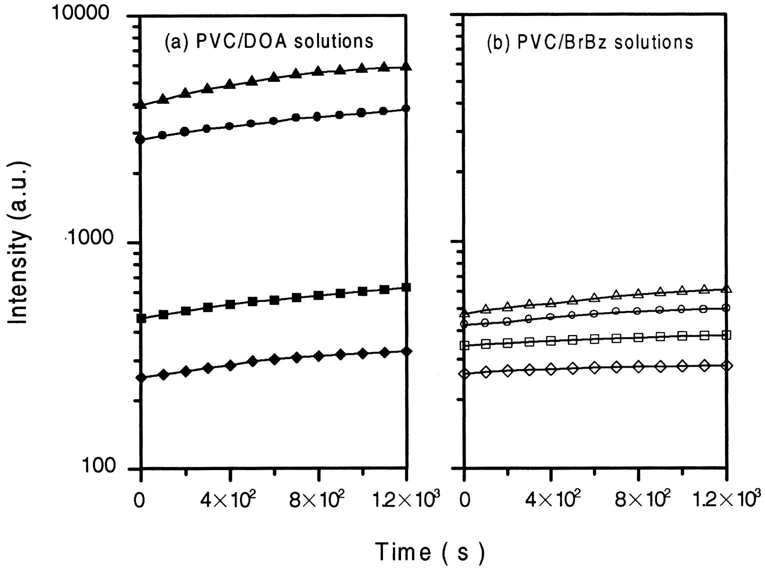

Fig. 6. Plots of the logarithm of scattered intensity at $\theta = 90°$ various aging time at 30°C for various PVC/DOA solution; (a) PVC/DOA solution; (b) PVC/BrBz solution. The PVC concentrations are 10, 5, 1.0, 0.5 g l^{-1} from the top for various PVC solutions.

chains occur first; then the gelation induced by connecting these aggregates results in the slower rate of gelation.

Recently, Matsuo et al. [18,19] have studied the phase separation behavior of PVA in DMSO/H_2O mixed solutions. Their results showed that the logarithm of light scattered intensity for PVA solution increased linearly with time in the initial stage of the phase separation. Generally, the phase separation of the solution exhibits pronounced optical heterogeneity, which results in an increase of the light scattered intensity. Fig. 6(a,b) shows the logarithm of the scattered intensity at $\theta = 90°$ ($q = 11.10\ \mu m^{-1}$) as a function of the time for PVC/DOA and PVC/BrBz solutions with various polymer concentrations at 30°C, respectively. The results indicate that the increment of scattered intensity with time of PVC/DOA solutions is larger than that of PVC/BrBz solutions. The linear increase in the scattered intensity with time may be described using the linear theory of spinodal decomposition proposed by Cahn [21] which is given as follows:

$$I(q,t) = I(q,t=0)\exp[2R(q)t] \quad (3)$$

where $I(q,t)$ is the scattered intensity at the time, t and $R(q)$ is the growth rate of concentration fluctuation as a function of scattering vector, q. Although many results [15–20] showed the $R(q)$ value changes with q, the only $R(q = 11.10\ \mu m^{-1}(\theta = 90°))$ value is presented as a reference for the qualitative discussion. $R(q)$ value could be also regarded as the rate of spinodal solution. The $R(q = 11.10\ \mu m^{-1})$ values for various PVC solutions are obtained from the slope of $\ln(I)$ versus t in Fig. 6 as shown in Fig. 7. The $R(q = 11.10\ \mu m^{-1})$ value in PVC/DOA solution increases significantly with increasing polymer concentration, while the lower $R(q = 11.10\ \mu m^{-1})$ value in PVC/BrBz solution shows no remarkable change. This result reveals clearly that PVC/DOA solutions exhibit a faster rate and more pronounced degree of spinodal decomposition than PVC/BrBz solutions. The spinodal decomposition induced by the thermodynamic driving force of the liquid–liquid phase separation proceeds with difficulty because of the strong polymer–solvent interaction, resulting in a comparatively homogeneous solution.

As stated in Fig. 5, the gelation time of PVC/BrBz solution is shorter than that of PVC/DOA solution at a given temperature and polymer concentration. However, the spinodal decomposition rate of PVC/BrBz solution is slower than that of PVC/DOA solution. These facts may be related

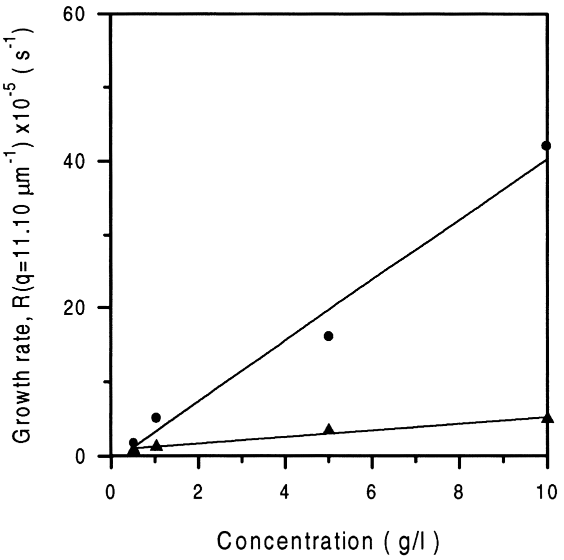

Fig. 7. Plots of the growth rate of concentration fluctuation, $R(q = 11.10\ \mu m^{-1})$ versus concentration for various PVC solutions at 30°C: (●) PVC/DOA solution; (▲) PVC/BrBz solution.

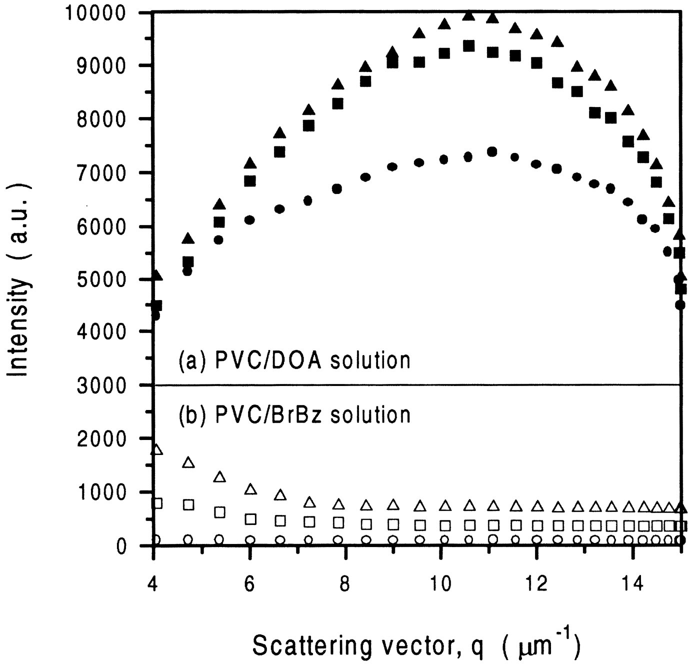

Fig. 8. Plots of the scattered profiles ($I(q)$ versus q) of PVC solutions ($C = 10$ g l^{-1}) with various aging time at 30°C: (a) PVC/DOA solution; (b) PVC/BrBz solution. The aging times are 600, 30, 5 min from the top for various PVC solutions.

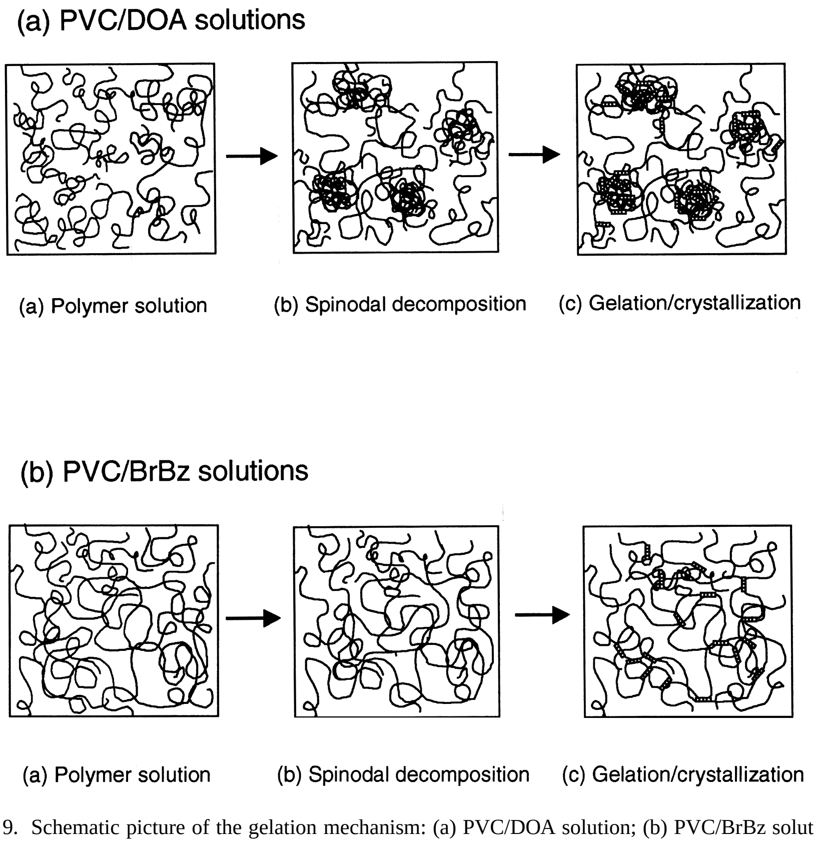

Fig. 9. Schematic picture of the gelation mechanism: (a) PVC/DOA solution; (b) PVC/BrBz solution.

to various gelation mechanisms between PVC/DOA and PVC/BrBz solutions. Generally, the rate of spinodal decomposition is proportional to the gelation time. Matsuo et al. [38] investigated the phase separation in PVA/DMSO/H_2O mixed solution by light scattering. They pointed out that phase separation at 50/50 vol% (DMSO/H_2O) composition is more significant than that at the 70/30 vol% composition at the same polymer concentration, and that the gelation and spinodal decomposition occur simultaneously. It is well known that the gelation in PVC solution is induced by the crystallization; then the microcrystals are formed as junction points in the gel network. Generally, the polymer solution exhibits the liquid–liquid phase separation, which is mainly related to the crystallization and the spinodal decomposition processes during cooling and aging. For PVC/BrBz solutions in the initial stage of phase separation, spinodal decomposition and gelation might occur simultaneously because the more extended chains in good solvent are advantageous to the intermolecular association for forming microcrystals/junction points. This gelation mechanism must result in a homogeneous gel network. On the contrary, the larger degree of spinodal decomposition must first occur to form the very heterogeneous solution because the poor solubility of the solvent used is more favorable to the intramolecular aggregation in PVC/DOA solutions. Subsequently, the crystallization takes place within the concentrated phase (polymer-rich phase) for the gelation. This gelation mechanism must form a heterogeneous gel.

Fig. 8(a,b) shows the scattered profiles ($I(q)$ versus q) as a function of aging time for PVC/DOA and PVC/BrBz solutions, respectively. A distinct scattering maximum appears in PVC/DOA solutions and the intensity of scattering maximum increases with increasing time, as shown in Fig. 8(a). The appearance of scattering maximum in PVC/DOA solution is attributed to the significant degree of the phase separation or the chain aggregation. On the other hand, Fig. 8(b) shows that no scattering maximum is found in PVC/BrBz solutions, and the scattered intensity is lower than that of PVC/DOA solution. All results clearly indicate that the chain aggregation or the phase separation of PVC/DOA solutions is more pronounced with increasing time than that of PVC/BrBz solutions.

Our previous study [1] showed that the X-ray scattering peak in PVC/DOA gel was much sharper than that in PVC/BrBz gel, indicating that PVC/DOA gel has a thicker network structure due to a larger degree of chain aggregation. The appearance of the scattering maximum in the PVC/DOA solution is considered due to a large degree of aggregation, resulting in the increase of the density and the size of the aggregate. Both the spinodal decomposition and the crystallization have been suggested as a primary role in gelation mechanism for many physical gels [39–41]. It should be noted from the thermodynamic theory that the crystallization cannot occur without the spinodal decomposition process [39]. From the discussions as stated above, we compared the gelation mechanism between PVC/BrBz and PVC/DOA solutions as shown in Fig. 9. Fig. 9(a) shows the gelation mechanism of PVC/DOA solution. The significant degree of spinodal decomposition due to the low polymer–solvent interaction first occurs where the polymer-rich and polymer-poor domains are present. Then, the crystallization takes place and many crystallites are presented inside these polymer-rich domains, which act as physical cross-links in the gel network. On the other hand, PVC/BrBz solution exhibits a much extended chain conformation and a smaller degree of spinodal decomposition, because of the high polymer–solvent interaction. The reason for making a dispersion of microcrystals/junction points is formed with direct crysallization accompanied by spinodal decomposition during gelation of PVC/BrBz solution. Mutin and Guenet [6] determined the morphologies of PVC gels using optical microscopy. They reported that the mesh size of network structure in PVC gel is about $5 \sim 10$ μm and the mesh size of PVC gel in good solvent is smaller than that in poor solvent. Our previous study [1] in PVC gels pointed out that PVC/BrBz gels had a higher elasticity than PVC/DOA gels. This is considered due to the homogeneous network structure with a smaller mesh size. The result corresponds to our previous studies in PVA gels [12]. The high crystalline and opaque gel formed from poor solvent, EG, exhibited a lower value of electricity compared with that of a lower crystalline and transparent gel formed from good solvent, NMP. Reconsidering the effect of the polymer–solvent interaction on the gelation mechanism, the gelation temperature of 30°C is much lower than the θ-temperature of PVC/DOA solution (ca. 68°C), where the high repulsive interaction has already existed to cause the large degree of spinodal decomposition of the solution. The increase in the intensity of scattering maximum must be contributed to the increase in a polymer-rich domain. At the same time the PVC/BrBz solution is cooled near the θ-temperature (ca. 32°C), the solution should exhibit no significant degree of spinodal decomposition. The crystallization induced by the intermolecular association must form a homogenous network structure and a transparent gel.

4. Conclusions

The effect of the polymer–solvent interaction on the aggregation behavior of PVC solutions was discussed in this work. The used solvents, BrBz and DOA, have a similar value of the solubility parameter. However, the affinity to PVC between these two solvents is quite different. The result in the Zimm plot of PVC solutions shows that PVC/BrBz solution has larger A_2 and R_g values than PVC/DOA solution at the same temperature. This fact means that the polymer–solvent interaction in PVC/BrBz solution is much higher than that in PVC/DOA solution. In other words, in PVC chains in good solvent, BrBz, must exhibit a more extended conformation. The result in the variation of R_g value with temperature shows that PVC/BzBz solution exhibits the coil–globule transition, while not any transition is observed in PVC/DOA solution in the measuring temperature range. This may be due to the much higher θ-temperature (ca. 68°C of PVC/DOA solution. The chain dimensions of PVC in poor solvent is comparatively difficult to change because of the low solubility. The difference between the critical gelation concentration, C^*, and the overlapping concentration, C_{Rg}^*, is found in both PVC/BrBz and PVC/DOA solutions. The chain overlapping concept cannot be suitable to this study because the gelation or the molecular aggregation behaviors may be caused by the phase separation from heterogeneous solution. The ΔC^* ($\Delta C^* = C^* - C_{Rg}^*$) value in PVC/DOA solution ($7.55\ \mathrm{g\ l^{-1}}$) is larger than that in PVC/BrBz solution ($3.91\ \mathrm{g\ l^{-1}}$), indicating that PVC/DOA solution must exhibit a larger degree of the liquid–liquid phase separation or the spinodal decomposition than PVC/BrBz solution does. The poor solubility of the solvent used should be more favorable to intramolecular aggregation of PVC chains, resulting in a comparatively heterogeneous solution. The gelation time of PVC/BrBz solutions is shorter than that of PVC/DOA solutions at all measuring concentrations. The larger R_g value of PVC/BrBz solution makes PVC chains become more extended to increase the opportunity of the intermolecular association for the gelation. On the other hand, the smaller R_g value of PVC/DOA solution may make the intramolecular association of PVC chains occur first, and then the gelation induced by connecting these aggregates results in the slow rate of gelation. The rate of spinodal decomposition of PVC solutions is estimated from the linear theory proposed by Cahn. The result shows that PVC/DOA solutions exhibit faster rate and more pronounced degree of spinodal decomposition than PVC/BrBz solutions. A distinct scattering maximum appears in PVC/DOA solutions and the intensity of scattering maximum increases with increasing time. The appearance of scattering maximum in PVC/DOA solution is attributed to the significant degree of the phase separation or the chain aggregation. On the other hand, no scattering maximum is found in PVC/BrBz solutions, and the scattering intensity is lower than that of PVC/DOA solution. All results clearly indicate that the chain aggregation or the phase separation of PVC/DOA solutions is more pronounced with increasing time than that of PVC/BrBz solutions. As a conclusion, the gelation mechanism of PVC solution is considered dominated by the competition between the crystallization and the spinodal decomposition rates. In the PVC/BrBz solution, the slighter degree of spinodal decomposition simultaneously accompanies the occurrence of the crystallization/gelation because the more extended chains in good solvent are advantageous to the intermolecular association for forming microcrystals/junction points. This mechanism must result in a homogeneous gel network. On the contrary, the larger degree of spinodal decomposition must first occur to form the much heterogeneous solution because the poor solubility of the solvent used is more favorable to the intramolecular aggregation in PVC/DOA solution. Subsequently, the crystallization takes place within the concentrated phase (polymer-rich phase) for the gelation. This gelation mechanism must form a heterogeneous gel.

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