Gelation Process and Phase Separation of PVA Solutions As Studied by a Light Scattering Technique

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Received April 12, 1999; Revised Manuscript Received August 26, 1999

ABSTRACT: Time-resolved light scattering measurements were performed on gelation processes of poly(vinyl alcohol) (PVA) solutions at 25 °C in mixtures of dimethyl sulfoxide (DMSO) and water (H_2O) with volume ratios of 60/40 and 80/20. It was found that the scattering profile $I(Q)$ from a 60/40 (DMSO/H_2O) solution has a maximum whose position Q_m is independent of time and that the intensity $I(Q)$ at $Q = Q_m$ increases exponentially with time. These observations agree with the theoretical predictions for the initial stage of spinodal decomposition (SD) type phase separation, while the scattering profile $I(Q)$ from a 80/20 solution has no peak. It is therefore concluded that the SD type microphase separation occurs before gelation in the 60/40 solution, but not in the 80/20 solution. On the basis of present, as well as past results, a possible mechanism of the gelation process for PVA solutions has been proposed.

1. Introduction

Polymer gels have been studied extensively from the point of view of fundamental science, as well as industrial applications, because they show many interesting features, such as being elastically soft and highly solvent absorptive.[1−5] Structural investigations of polymer gels are absolutely necessary to give the bases for many applications. However, quantitative studies on the gel structure are not enough, especially from microscopic points of view. One of the reasons is that polymer gels often have hierarchic structures extending in a very wide spatial scale as was preliminarily shown in a previous paper.[6]

In the series of studies on poly(vinyl alcohol) (PVA) gels formed in mixtures of dimethyl sulfoxide (DMSO) and water,[7−10] we constructed a macroscopic sol−gel diagram and observed the turbidity of the gels as functions of PVA concentration and temperature.[7] It was found that the PVA gels from solutions of a binary mixture of 60/40 (v/v) DMSO/H_2O are opaque when they are formed above about −20 °C, and they are transparent below −20 °C. In addition, the crossover concentration of the sol−gel transition C_g* is independent of gelation temperature below −20 °C, which agrees with the overlapping concentration C_{R_g} of PVA chains having an average radius of gyration R_g while it is lower than a C_{R_g} above −20 °C. From these macroscopic observations, it is expected that microphase separation takes place in the PVA gel above −20 °C.

With the intention of revealing the microscopic structure, we performed wide- and small-angle neutron scattering (WANS and SANS) measurements on the PVA gels produced from mixtures of DMSO/water with volume ratios of 60/40 and 80/20 at 25 °C;[10,11] the former gels were opaque, and the latter ones were transparent. In the WANS measurements, a few weak but clear crystalline diffraction peaks characteristic of PVA crystals were observed and disappeared coincidentally with melting of the gel, supporting that the cross-linking points of the gel are crystallites. It was found in the SANS measurements that the Q dependence of the scattering intensities $I(Q)$ from the transparent gels with the 80/20 mixture solvent can be well-described by the Ornstein−Zernike (OZ) formula in a Q range of 3×10^{-3} to 5×10^{-2} Å^{-1}, whereas the opaque gels show an excess scattering intensity, deviating from the OZ formula below $Q = 8 \times 10^{-3}$ Å^{-1}. This suggests that the latter has a larger structure than that of the concentration fluctuations due to network structure, i.e., the mesh size of network. It was presumed that the excess scattering is brought about by the inhomogeneity caused by the spinodal decomposition (SD) type microphase separation. In addition to the 60/40 (DMSO/water) solution of PVA, such microphase separation was also suggested in gels from aqueous solutions[12,13] as well as in those from ethylene glycol and propylene glycol solutions.[14]

In this work, to confirm directly whether the SD type microphase separation actually occurs in the formation process of the opaque gel, we perform time-resolved light scattering (LS) measurements in the gelation processes of PVA solutions in the DMSO/water mixtures with a volume ratio of 60/40, and for comparison, we do similar measurements on the transparent gels produced from the 80/20 solution.

2. Experimental Section

2.1. Materials. Fully saponified atactic PVA with a number-average degree of polymerization of $P_n = 1700$ and a molecular weight distribution of $M_w/M_n = 1.97$ was used for the LS measurements. The details of characterization of this PVA sample was reported elsewhere.[7] The solvents used for the scattering experiments were mixtures of DMSO and water with volume ratios of 60/40 and 80/20, which will thereafter be indicated 60/40 and 80/20 (DMSO/H_2O) solvents, respectively.

Gel samples were prepared as follows. A given amount of PVA was dissolved in the solvent at about 130 °C to be homogenized in a glass tube, and then, the solution was filtered through a 0.22 μm Millipore filter in a dust-free cylindrical Pyrex cell with an inner diameter of 10 mm. Just before the measurements, the samples in the cell were again homogenized at 100 °C for about 30 min and quenched to the measuring temperature at 25 °C. In this work, the PVA concentration was 5 g/dL for all cases. Gelation time was measured just after quenching the solution from 100 to 25 °C,

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10.1021/ma990565j CCC: $18.00
Published on Web 10/20/1999

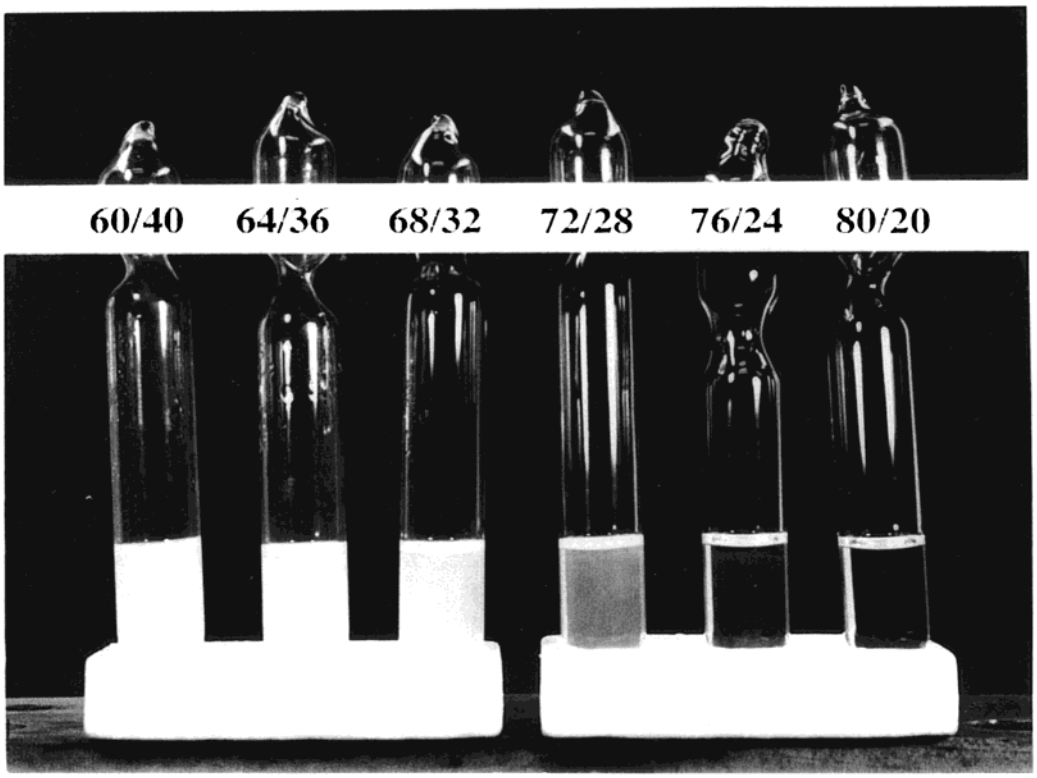

Figure 1. Photograph of PVA gels in mixtures of DMSO and water with volume ratios of 60/40, 64/36, 68/32, 72/28, 76/24, and 80/20. The PVA concentration of these gels was 5 g/dL, and the gelation temperature was 25 °C.

and the sol−gel transition point was determined macroscopically by a ball-falling method; the detail of this method was previously reported.[8]

2.2. Measurements. Light scattering (LS) measurements were carried out with a System 4700 from Malvern Instruments, Inc., using an Ar^+ laser ($\lambda = 488$ nm, 75 mW) as a light source. The length of scattering vector $Q = 4\pi n \sin\Theta/\lambda$, n being the reflective index, is in a range of 3.6×10^{-4} to 3.6×10^{-3} Å^{-1}. The absolute intensity (Rayleigh ratio) was calculated using toluene as a standard to be $R_{tol} = 39.6 \times 10^{-6}$ cm^{-1} for $\lambda = 488$ nm at $T = 25$ °C.[15] To reduce the effect of inhomogeneity (speckle) of samples,[16] which arises from the gel structure itself, the measurements were mainly performed by rotating a sample cell (10 mm ϕ) at a frequency of 0.5 to 5 rpm. The inhomogeneity of the gels will be briefly discussed in the next section.

Time-resolved LS measurements were carried out just after transferring the solution at 100 °C to a sample cell holder which had been kept at a given temperature. The 60/40 solutions gradually become opaque with time, and the measurements were continued until transmittance of incident light decreased to 80% for the 10 mm optical path. In this work, it was found that the effect of the multiple scattering is not serious up to 90% transmittance. Hence, the quantitative discussion was limited to samples being 90% transmittance.

3. Results and Discussion

3.1. Transparent and Opaque Gels. PVA solutions in mixtures of DMSO and water with volume ratios ranging from 60/40 to 80/20 and homogenized at 100 °C were quenched to 25 °C and allowed to gel for 24 h. A photograph of the gels is shown in Figure 1. The gel is completely opaque when it is produced from the 60/40 mixture solvent, but it becomes translucent with increasing the DMSO ratio in the mixture; with 80/20, it is almost transparent. It is obvious from the appearance of opaqueness that the 60/40 DMSO/H_2O gel has some structure scattering light that may be in a spatial scale of submicrometer to micrometer. In the previous papers,[7,10] we considered that this structure was caused by an SD type microphase separation on the basis of the results of the sol−gel diagram[7] as well as the upturn[10] in the SANS intensity observed below $Q = 0.008$ Å^{-1}. To show directly that this structure is due to the SD type microphase separation, we have performed LS measurements on the 60/40 and 80/20 DMSO/H_2O solutions of PVA, which grow to opaque and transparent gels, respectively.

3.2. Inhomogeneity of Gels. As described above, the opaque 60/40 gel is extremely inhomogeneous in size, compared with the wavelength of light. However, it should be noted that even the transparent 80/20 gel is inhomogeneous compared with the solution homogenized at 100 °C. This is demonstrated in what follows.

The time evolution of LS intensity measured at a scattering angle of 60° for the 80/20 solution after the temperature jump from 100 to 25 °C is shown in Figure 2, where the intensities measured with and without rotating the sample cell are indicated. The scattering intensity measured without rotating the cell greatly fluctuates in space and time after gelation, although the fluctuations begin to increase even before microscopic gelation; the gelation time (=330 min) is indicated by an arrow in Figure 2. This suggests that the gel is very inhomogeneous in space and time compared with the sol. On the other hand, the scattering intensity observed with rotating the sample cell increases smoothly with time, meaning that the intensity fluctuations are averaged out in space by rotating the cell. Thus, the rotation corresponds to taking an ensemble average of the system. The intensity fluctuations are originated from the so-called speckle,[16] which gives useful information about the inhomogeneity of gels.[17,18] However, such inhomogeneity is out of the scope in this paper. Hence, we performed the LS measurements with rotations of

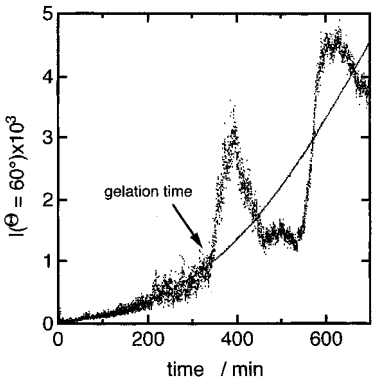

Figure 2. Time evolution of the LS intensity of a PVA solution with a concentration of 5 g/dL in a mixture of DMSO and water (80/20, v/v) just after a homogeneous solution at 100 °C was quenched to 25 °C. The intensities were measured at a scattering angle of 60° with (—) and without (·····) rotating the sample cell. The gelation time is indicated by an arrow.

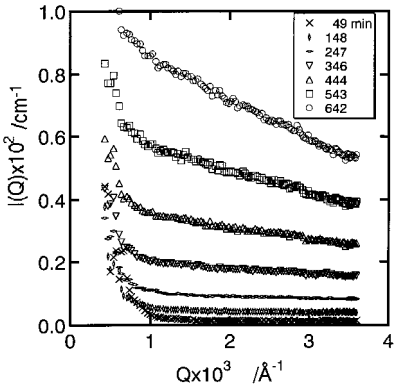

Figure 3. Time evolution of the LS scattering profile $I(Q)$ of a PVA solution with a concentration of 5 g/dL in a mixture of DMSO and water (80/20, v/v) just after a homogeneous solution at 100 °C was quenched to 25 °C.

the sample cell to see the averaged structure of sols and gels. The increase of the averaged scattering intensity with time for the 80/20 solution may not be caused by the microphase separation, but by the concentration fluctuations according to the gel network formation as will be discussed later.

3.3. Time-Resolved LS Measurements during the Gelation Process. Time-resolved LS measurements have been carried out on the 80/20 and 60/40 solutions of PVA just after a temperature jump from a homogeneous solution at 100 °C to given temperatures. The data acquisition time required for one measurement of the Q-dependent scattering profile from 3.6×10^{-4} to 3.6×10^{-3} Å^{-1} was 2.5 min, which is short enough to observe the time evolution of the scattering profile. The time evolutions of the light scattering profiles $I(Q)$ for the 80/20 and 60/40 solutions quenched and measured at 25 °C are shown in Figures 3 and 4, respectively. Note that the intensity scale in Figure 3 for the 80/20 solution is expanded by a factor of 40. The gelation times determined by a ball-falling method[8] are 330 and 180 min for the 80/20 and 60/40 solutions at 25 °C, respectively, meaning that both scattering profiles shown in Figures 3 and 4 mainly correspond to those for sols. The scattering intensity from the 80/20 solution is very weak compared with that from the 60/40 solution; the intensity of the former at the gelation time (= 330 min) was about 100 times smaller than that of the latter at around $Q = 1 \times 10^{-3}$ Å^{-1}. This very large intensity

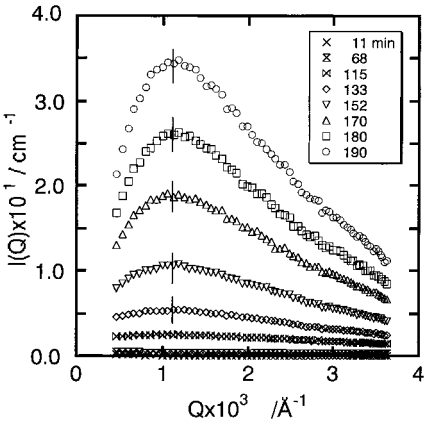

Figure 4. Time evolution of the LS scattering profile $I(Q)$ of a PVA solution with a concentration of 5 g/dL in a mixture of DMSO and water (60/40, v/v) just after a homogeneous solution at 100 °C was quenched to 25 °C.

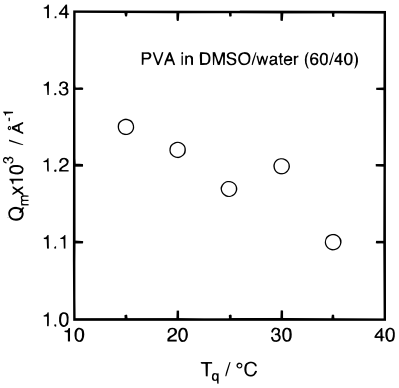

Figure 5. Peak position Q_m as a function of annealing temperature for a PVA solution with a concentration of 5 g/dL in mixture of DMSO and water (60/40, v/v).

difference cannot be explained by the negligibly small difference (less than ~3%) between refractive indices of the two solutions. The intensity of the 80/20 solution is too small to assign to the increase of the intensity to the microphase separation, but it may be assigned to the concentration fluctuations due to the network formation itself. This picture is also supported by the fact that the scattering profile $I(Q)$ of the 80/20 solution does not have a peak characteristic of an SD type microphase separation. On the other hand, the scattering profile $I(Q)$ of the 60/40 solution shows a very strong peak at $Q_m = 1.2 \times 10^{-3}$ Å^{-1} at 25 °C, which may correspond to a characteristic wavelength of 0.53 μm ($=2\pi/Q_m$) of the SD type microphase separation as was reported in the previous papers.[7,10]

The time evolution of the scattering profile $I(Q)$ provides further useful information. As seen in Figure 4, the peak position Q_m of $I(Q)$ is almost time-independent until 190 min. Similar results were obtained at annealing temperatures of 15, 20, 30, and 35 °C. The values of Q_m as a function of annealing temperature are shown in Figure 5; Q_m decreases with increasing annealing temperature, meaning that the characteristic wavelength of SD increases with temperature. In Figure 6, the intensity at the maximum position $I(Q_m)$ is also plotted as a function of annealing time in a semilogarithmic form; the arrows indicate the gelation times determined by a ball-falling method. Before the gelation time, the intensities $I(Q_m)$ increase exponentially with time, which agrees with the SD theory, but their growth

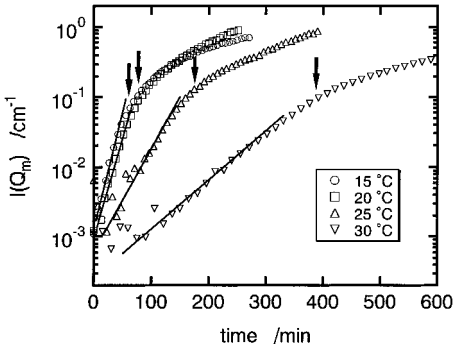

Figure 6. Time evolution of the intensity $I(Q_m)$ for a PVA solution with a concentration of 5 g/dL just after a homogeneous solution at 100 °C was quenched to 25 °C. Gelation times are indicated by arrows.

rates slow near the macroscopic gelation times. Such slowing is considered to be due to network formation by gelation. Here, it should be noted that the gelation occurs only in the concentrated regions produced by the microphase separation causing a bicontinuous structure[19] because the concentration of the dilute region is very small in the case of polymers. Accordingly, the network formation does not perfectly suppress the growth of microphase separation, which is clear from Figure 6; a considerable increase of $I(Q_m)$ is still observed for every case even after gelation.

3.4. Mechanism of the Phase Separation. As shown above and from Figures 4 and 6, we experimentally observed the following results for the 60/40 solution of PVA: (1) there is a maximum in the LS profile $I(Q)$, (2) the maximum position Q_m is independent of time, and (3) the maximum intensity $I(Q_m)$ increases exponentially with time. The most plausible origin of these observations is the SD type microphase separation. According to the well-known linearized kinetic theory for phase separation presented by Cahn and Hilliard,[20,21] the growth rate of the concentration fluctuations is given by

$$R(Q) = -DQ^2\left\{\left(\frac{\partial^2 f}{\partial C^2}\right) + 2\kappa Q^2\right\} \tag{1}$$

where C, D, f, and κ are polymer concentration, translational diffusion coefficient, free energy density of the system, and a positive constant, respectively. In the unstable region where $\partial^2 f/\partial C^2$ is negative, the growth rate can be positive in some Q region. In such Q regions, the concentration fluctuations grow spontaneously with time, and spinodal decomposition occurs. The growth rate has a maximum at a wavenumber Q_m,

$$Q_m^2 = -(\partial^2 f/\partial C^2)/4\kappa \tag{2}$$

and the time evolution of the scattering intensity is described by

$$I(Q,t) = I(Q,0)\exp[2R(Q)t] \tag{3}$$

It is obvious from eqs 1−3 that (i) the scattering intensity $I(Q)$ has a maximum at a characteristic wavenumber Q_m for the concentration fluctuations, (ii) the characteristic wavenumber Q_m is time-independent, and (iii) the amplitude of the concentration fluctuations grows exponentially with time. These predictions actually agree with the experimental observations 1−3 described above, concluding that the SD type phase separation occurs in the early stage of the gelation process for the 60/40 solution of PVA.

Next, let us consider the effect of annealing temperature T_q on the maximum position Q_m. By describing the free energy density f of eq 2 in terms of the Flory−Huggins formula, the temperature dependence of the maximum wavenumber Q_m is theoretically given by[22]

$$Q_m = \frac{1}{L}\left[\frac{3|T_s - T|}{T_s}\right]^{-1/2} \tag{4}$$

where L and T_s are the interaction distance and the spinodal temperature, respectively, at concentration C, and it was assumed that the temperature dependence of the Flory−Huggins interaction parameter χ is given by $\chi = \chi_h/T$. In the present system, it is unfortunately hard to determine the spinodal temperature precisely because the phase separation and the gelation occur simultaneously. Hence, quantitative comparison is impossible, but eq 4 qualitatively explains the temperature dependence of Q_m; i.e., the characteristic wavenumber increases with decreases in the quenching depth $|T_s - T|$. This qualitative prediction accords with that observed; Q_m decreases with $T \equiv T_q$, as seen from Figure 5.

3.5. Mechanism of Gelation. Finally, we discuss the gelation mechanism of the 80/20 and 60/40 solutions. In the 60/40 solution, the SD type microphase separation occurs before the macroscopic gelation, resulting in formation of a bicontinuous structure of concentrated (polymer-rich) and diluted (polymer-poor) phases. This is schematically illustrated in Figure 7. The PVA concentration in the concentrated phase is larger than the initial PVA concentration before the phase separation. The cross-linking points, which are the crystallites in this system,[9] are preferably formed in the concentrated phase, spreading bicontinuously over the whole

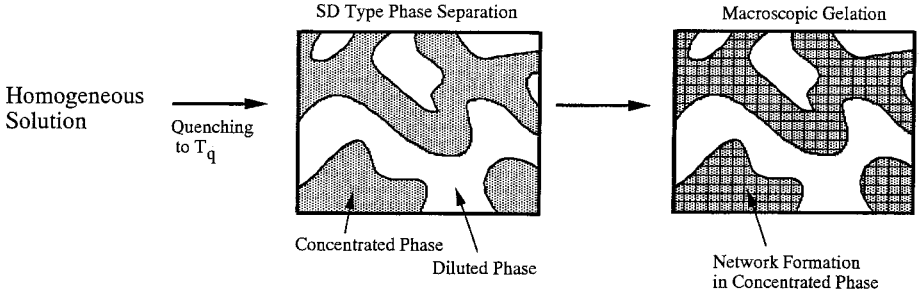

Figure 7. Schematic sketch of gelation process of a PVA solution in mixture of DMSO and water (60/40, v/v) at 25 °C. In the early stage of the gelation, the spinodal decomposition type microphase separation occurs, and then, network formation takes place by crystallization, i.e., the formation of crystallites, some of which work as cross-linking points in the bicontinuous concentrated (polymer-rich) phase.

system. The network formation in the concentrated phase results in the macroscopic gelation accompanying the inhomogeneity due to the SD type microphase separation, which makes the gel opaque. On the other hand, in the case of the 80/20 solution, phase separation does not occur, and hence, the homogeneous solution gels as a whole to form the infinite network, resulting in a transparent gel.

4. Conclusion

In this work, we have performed time-resolved LS measurements on the gelation process of PVA solutions in mixtures of DMSO and water with volume ratios of 80/20 and 60/40, which form transparent and opaque gels, respectively. It was observed for the 60/40 solution that (1) the scattering profile $I(Q)$ has a maximum at Q_m, (2) the maximum position Q_m is independent of time, and (3) the intensity $I(Q)$ at a constant Q including Q_m increases exponentially with time. These observations agree with the theoretical predictions of the linearized theory of Cahn and Hilliard, leading to the conclusion that in the case of the 60/40 solution the SD type microphase separation occurs in the early stage of the gelation process. In this case it is therefore considered that microphase separation occurs first, and then, the network is formed in the bicontinuous concentrated phase spreading over the system. As a result, the opaque gel is formed macroscopically.

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