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Effects of cononsolvency on gelation of poly(vinyl alcohol) in mixed solvents of dimethyl sulfoxide and water

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Abstract

We studied the rates of gelation and phase separation of poly(vinyl alcohol) (PVA) solutions in mixtures of dimethyl sulfoxide (DMSO) and water at 25 °C and found that both the rates show a maximum at a volume fraction of DMSO $\phi_{DMSO} = 0.60$ while gelation was not observed either in pure DMSO or pure water, suggesting that water–DMSO is a cononsolvent system for PVA. On the basis of the data by Cowie [Can J Chem 36 (1961) 2240] we concluded that the 1:2 stable complex between one DMSO molecule and two water molecules is the main cause of this cononsolvency.

Keywords: Poly(vinyl alcohol); Gels; Cononsolvency

1. Introduction

In a series of papers [1–10], we have studied structure and formation process of poly(vinyl alcohol) (PVA) gels in mixed solvents of dimethyl sulfoxide (DMSO) and water, especially focusing on two mixed solvents with volume ratios 60/40 and 80/20. The structure and gelation rate strongly depend on the mixing ratio. In a mixture with volume fraction of DMSO $\phi_{DMSO} = 0.6$ gelation occurs rapidly at 25 °C after quenching from a homogeneous solution at 100 °C, resulting in an opaque gel while in a mixed solvent with $\phi_{DMSO} = 0.8$, the gelation rate is very slow compared with that for $\phi_{DMSO} = 0.6$ and the resultant gel is almost transparent. Regarding a cause of the turbidity, light scattering studies on the gelation process [9] have revealed that the spinodal decomposition (SD) type phase separation occurs before the network formation (gelation) for a solution with $\phi_{DMSO} = 0.60$. It is obvious that the solvent composition affects the gelation process. It should be noted that gelation of PVA is not observed either in pure water or in pure DMSO.[1] These results mean that mixing of two good solvents makes a poor solvent for PVA. Such phenomenon is known as cononsolvency [11–16].

In this study we have examined the gelation rate as well as phase separation rate as a function of the solvent composition. Taking into account that the phase separation rate reflects the phase diagram, we will discuss the effects of the solvent composition on the gelation in terms of cononsolvency, and consider the molecular origin of the cononsolvency. The concept of cononsolvency is very useful for systematic understanding of the gelation of PVA in mixtures of DMSO and water.

2. Experimental section

Fully saponified atactic PVA with a number-average degree of polymerization $P = 1730$ was used in this work. The molecular weight distribution M_w/M_n is 1.97 where M_w and M_n are weight- and number-average molecular weights, respectively. The details of the characterization of this sample were reported elsewhere [1]. The solvents used for the experiments were mixtures of DMSO and water with volume fraction of DMSO $\phi_{DMSO} = 0.0$, 0.10, 0.20, 0.30, 0.40, 0.50, 0.60, 0.64, 0.68, 0.72, 0.76, 0.80, 0.90 and 1.0.

Gel samples were prepared as follows. A given amount of PVA was dissolved in a solvent at about 130 °C in an autoclave to be homogenized in a glass tube and then the

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[1] Gel formation of a PVA aqueous solution depends on temperature T, concentration C_p of PVA and degree of polymerization P of PVA. Here we mean that gelation dose not occur under the present condition of $C_p = 5$ g/dl, $T = 25$ °C, and $P = 1730$.

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solution was filtered through a 0.45 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 25 °C for gelation. PVA concentration C_p was 5 g/dl for all cases.

Gelation time t_{gel} after quenching the solution from 100 to 25 °C was determined macroscopically by a tilting method [1]. Transparency of the gel was evaluated as a function of annealing time at 25 °C by measuring transmittance of visible light with wavelength of 488 nm. The measurements were carried out using a double-beam spectrophotometer Hitachi-220. A quartz cell with size 10 mm × 10 mm × 50 mm was used in this measurement.

3. Results and discussion

Gelation time t_{gel} of PVA solution at 25 °C was determined as a function of volume fraction of DMSO ϕ_{DMSO}. When $\phi_{DMSO} = 0.0$, 0.10, 0.20, 0.90 and 1.0, gelation was not macroscopically observed at least until 20,000 min after temperature jump to 25 °C. The shortest gelation time t_{gel} of 178 min was observed for $\phi_{DMSO} = 0.64$ and the longest one is 15,019 min, being about 10.4 days, for $\phi_{DMSO} = 0.30$. The gelation time strongly depends on the volume fraction of DMSO. Defining inverse of the gelation time t_{gel}^{-1} as a gelation rate, it is plotted as a function of volume ratio of DMSO ϕ_{DMSO} in Fig. 1. The gelation rate increases extremely by adding DMSO to water until around $\phi_{DMSO} = 0.60$ and then decreases with further addition of DMSO. As mentioned above, in both pure DMSO and pure water gelation does not occur under the present experimental condition, showing that both are rather good solvents for PVA. In other words, mixing of two good solvents forms a poor solvent, suggesting that water–DMSO is a cononsolvent system for PVA.

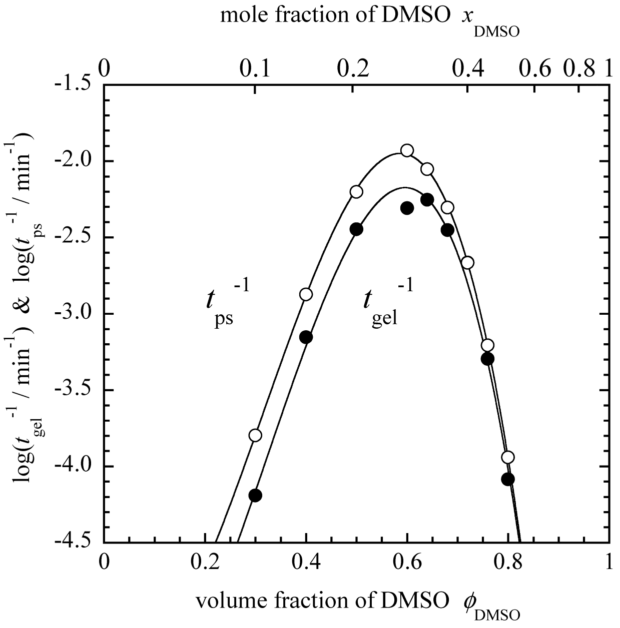

Fig. 1. Rate of gelation t_{gel}^{-1} (●) and rate of phase separation t_{ps}^{-1} (○) for the PVA solutions at 25 °C after temperature jump from 100 °C as a function of the volume fraction of DMSO ϕ_{DMSO}. PVA concentration C_p is 5 g/dl.

As reported before [7], SD type phase separation occurs before gelation in the PVA solution with $\phi_{DMSO} = 0.60$, resulting in polymer-rich and polymer-poor phases. The network formation or the formation of cross-linking points, which are crystallites [4] in this PVA solution, occurs mainly in the polymer-rich phase, meaning that overall gelation rate in Fig. 1 must be affected by the phase separation process. On the other hand, rate of the phase separation is hardly affected by the gelation because it occurs before the gelation. We therefore estimated the rate of phase separation as a function of the volume fraction of DMSO to see effects of cononsolvency only on the phase separation.

Transmittance of light through the PVA solution was continuously monitored after temperature jump from 100 to 25 °C. The PVA solutions become gradually opaque with annealing time in a ϕ_{DMSO} range between 0.3 and 0.8 while those with $\phi_{DMSO} = 0.0$, 0.10, 0.20, 0.90 and 1.0 do not, suggesting that liquid–liquid phase separation occurs in the limited region of ϕ_{DMSO}. The time evolution of the transmittance is shown for $\phi_{DMSO} = 0.30$, 0.40, 0.50 and 0.60 in Fig. 2(a), and for $\phi_{DMSO} = 0.64$, 0.68, 0.72, 0.76 and 0.80 in Fig. 2(b), respectively. The transmittance decreases the most rapidly for $\phi_{DMSO} = 0.60$ and the most slowly for

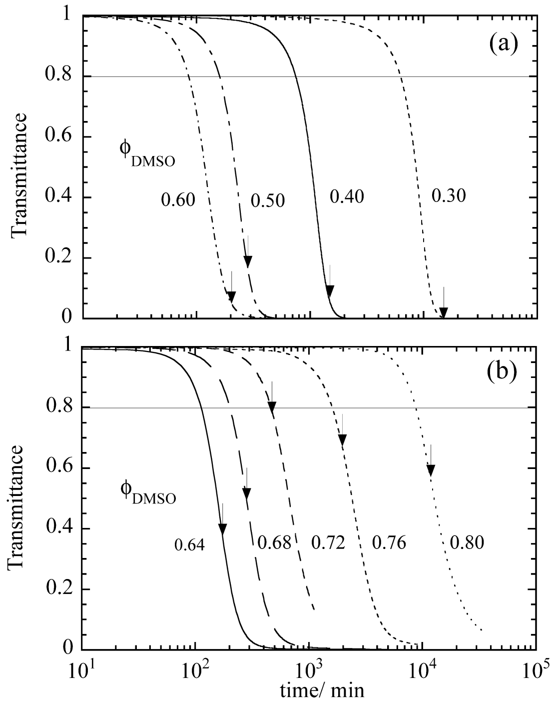

Fig. 2. Time evolution of light transmittance through the PVA solution at 25 °C after temperature jump from 100 °C (a) for $\phi_{DMSO} = 0.30$, 0.40, 0.50 and 0.60, (b) for $\phi_{DMSO} = 0.64$, 0.68, 0.72, 0.76 and 0.80. Arrows show the corresponding gelation time t_{gel}.

$\phi_{DMSO} = 0.80$ as seen in Fig. 2(a) and (b). Arrows in the figure show the gelation times t_{gel}. In any solutions, the transmittance begins to decrease before the gelation, confirming that the gelation hardly affects the phase separation process, at least, at 25 °C.

It is well known that the rate of phase separation can be precisely evaluated using a time-resolved light scattering technique [7], but in this work we have employed a conventional method. The mechanism of the phase separation is a SD type one as revealed in the previous paper [7]. The rate of the SD type phase separation in the early stage can be well described by the Cahn–Hilliard theory [17,18]. According to the theory, the scattering intensity due to the concentration fluctuations grows exponentially. If we assume that the rate of phase separation is independent of time, it can be shown that a time t_T at which the transmittance of light reaches a certain value T is inversely proportional to the rate of phase separation $R(Q)$. In this work, therefore, we have employed inverse of the time t_T at transmittance $T = 0.8$ as the rate of phase separation t_{ps}^{-1}.

Horizontal lines in Fig. 2(a) and (b) indicate transmittance $T = 0.8$. Values of t_{ps} are estimated from the intersection with this line and the rate of phase separation t_{ps}^{-1} is plotted in Fig. 1 as a function of the volume fraction of DMSO ϕ_{DMSO}. The rate has a maximum at around $\phi_{DMSO} = 0.60$ and this ϕ_{DMSO} dependence is similar to that of the gelation rate t_{gel}^{-1}, suggesting that the cononsolvency accelerate the network formation and the phase separation in a similar manner.

Cononsolvency effects are often discussed in terms of phase diagram. One of the examples has been reported [15,16] for poly(*N*-isopropylacrylamide) (PNIPAAM) in mixture of water and methanol. PNIPAAM is soluble in water at room temperature, and the solution undergoes phase separation upon heating at the lower critical solution temperature (LCST), which is 32 °C. Addition of methanol, which is a good solvent for PNIPAAM, lowers LCST and the lowest LCST is observed at the molar fraction of 0.35 while further addition raises it again. This means that the mixture with methanol fraction of 0.35 is the poorest solvent.

In the present study, we did not determine the phase diagram of the PVA solution in mixtures of DMSO and water, but the phase separation rate. It is known that the PVA solution has the upper critical solution temperature (UCST) [9], but it is hard to determine the exact phase diagram because the gelation or the network formation occurs simultaneously with the phase separation. However, it can be qualitatively shown that the rate of the phase separation reflects the phase diagram: the faster the phase separation rate the higher the UCST, and hence it is considered that the ϕ_{DMSO} dependence of the phase separation rate reflects that of the phase diagram. This allows us to discuss the cononsolvency effects on the rate from static structural or thermodynamic points of view.

As seen in Fig. 1, the mixture with $\phi_{DMSO} = 0.60$ is the poorest solvent for PVA. This can be understood from the nature of mixture of water and DMSO, which has been extensively studied by Cowie et al. [19]. They measured the viscosity, density and heat of mixing as a function of volume fraction of DMSO ϕ_{DMSO}, and found that the viscosity isotherm has a positive maximum at a volume fraction of DMSO $\phi_{DMSO} = 0.68$ and the heat of mixing has a flat maximum between $\phi_{DMSO} = 0.51$ and 0.83. On the basis of these observations, they concluded that a stable 1:2 association complex, corresponding to $\phi_{DMSO} = 0.66$, is formed between one DMSO molecule and two water molecules due to hydrogen bonds. This nature easily explains the ϕ_{DMSO} dependence of the phase separation rate (Fig. 1). PVA is soluble in pure water due to the formation of hydrogen bonds between hydroxyl groups in PVA and water molecules. When the molar fraction of DMSO is less than 0.33 ($\phi_{DMSO} = 0.66$), the added DMSO molecules form a 1:2 association complex with water molecules, and the excess water molecules form hydrogen bonds with hydroxyl groups in PVA to solve PVA. With increasing the fraction of DMSO, number of water molecules captured by DMSO increases and less water molecules participate in hydrogen bond formation with PVA. When the molar fraction of DMSO is 0.33 ($\phi_{DMSO} = 0.66$), all DMSO molecules form a 1:2 association complex with two water molecules and no hydrogen bonds with PVA are formed.[2] This mixture is the poorest solvent. As the fraction of DMSO further increases, excess DMSO molecules can form hydrogen bonds with PVA so that the mixture becomes better solvent than a mixture with $\phi_{DMSO} = 0.66$. In this experiment, the maximum rate of the phase separation is observed at $\phi_{DMSO} = 0.60$, showing that this mixture is the poorest solvent. The fraction ($\phi_{DMSO} = 0.66$) for the stable 1:2 complex is close to the fraction for the poorest solvent ($\phi_{DMSO} = 0.60$), leading to a conclusion that the 1:2 stable complex is the main cause of this cononsolvency. At the moment, however, the small difference between the fraction for the poorest solvent $\phi_{DMSO} = 0.60$ for PVA and the fraction for the most stable complex $\phi_{DMSO} = 0.66$ between DMSO and water is not clear.

4. Conclusion

We have estimated the gelation rate t_{gel}^{-1} and the rate of phase separation t_{ps}^{-1} of PVA solutions in mixtures of DMSO and water at 25 °C as a function of the volume fraction of DMSO. It was revealed that there are strong composition dependences on the gelation rate t_{gel}^{-1} as well as the rate of phase separation t_{ps}^{-1}. Both of them have a maximum at

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[2] Exactly speaking, ratio of hydrogen bonds among DMSO–water, DMSO–PVA and water–PVA is determined by the Boltzmann distribution.

around the volume fraction of DMSO $\phi_{\mathrm{DMSO}} = 0.60$, suggesting that the mixture with $\phi_{\mathrm{DMSO}} = 0.60$ is the poorest solvent for PVA. This means that water–DMSO is a cononsolvent system for PVA. On the basis of the data by Cowie [19] we have concluded that the 1:2 stable complex between one DMSO molecule and two water molecules is the main cause of this cononsolvency.

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