Gelation of poly(vinyl alcohol) in dimethyl sulfoxide/water solvent

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SUMMARY

Gelation of poly(vinyl alcohol) (PVA) in dimethyl sulfoxide (DMSO)/water was observed at 23 °C with viscometry, spectrophotometry, wide angle X-ray scattering and light scattering. Here transparent gel formation was found to take place prior to being turbid in some cases, whereas the solution became turbid prior to gelation in other cases. Whether transparent gel is formed at first or solution becomes turbid, depends on DMSO composition. PVA solution forms gel in the DMSO composition range from 20 to 80 wt.%. Below the boundary DMSO composition of 60-70 wt.%, gelation takes place at first (i.e. transparent gel is formed) and then becomes turbid eventually, while beyond this DMSO composition the solution becomes turbid and then opaque gel is formed.

INTRODUCTION

Poly(vinyl alcohol) (PVA) solution is able to form gel in various solvents. Recently, much attention[1-3] was paid to the gelation of PVA in dimethyl sulfoxide (DMSO)/water mixed solvent since it was reported that PVA gel in the mixed solvent was suitable for spinning high-tenacity/high-modulus PVA fiber. PVA solution in DMSO/water mixed solvent forms strong gel by repeating freezing-thawing cycle[2], or with increasing the degree of saponification of PVA over 96 mol%[2]. Transparent gel is formed below -20 °C, while opaque gel beyond -20 °C at 60 vol.% DMSO composition[3]. At room temperature, PVA solution forms opaque gel. Varying DMSO composition, however, some PVA/DMSO/water system is observed to form transparent gel even at room temperature. The gelling process of PVA solution is so complicated that its mechanism has not been clarified sufficiently.

In this report, gelation and turbidity of the PVA solution in DMSO/water mixed solvent was observed at 23 °C as a function of time by means of viscometry, spectrophotometry, wide angle X-ray scattering and light scattering, where the concentrations of PVA and/or DMSO were varied. The PVA structural change upon gel formation will be discussed from the morphological point of view.

EXPERIMENTAL PART

Sample Preparation

PVA sample was purchased from Nacalai Tesque, Inc. (Kyoto, Japan), and re-saponified. The degree of polymerization was 1770 as estimated from the intrinsic viscosity[4], and the degree of saponification was found to be 99.5 mol% from titration using NaOH aqueous solution.

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Guaranteed reagent grade dimethyl sulfoxide (DMSO) (Nacalai Tesque, Inc.) was used without further purification.

A mixture of DMSO/water was prepared as solvent for PVA, where DMSO compositions were varied from 0 wt.% to 100 wt.% by the step of 10 wt.%.

PVA solutions were prepared by dissolving PVA in each DMSO/water mixture at 90 °C with the PVA concentration adjusted to 1, 2, 3, 4 and 5 wt.%, and then quickly quenched to 23 °C within 1 min. The PVA solutions prepared as mentioned above were employed in the following measurements at 23 °C.

Wide Angle X-ray Scattering and Light Scattering

The wide angle X-ray scattering (WAXS) measurements were performed by recording scattered intensities with a goniometer (PW1050, Phillips Co., Holland) under the applied power of 45 kV and 40 mA, where Mokα (λ=0.71Å) was employed as an incident beam in this study instead of conventional Cukα. Mass absorption coefficients (μ/ρ) of sulfur in DMSO for Cukα and Mokα are 90.0 and 9.9, respectively[5], and thus it is not possible to observe scattering intensity from solution containing more than 30 wt.% DMSO composition by using Cukα incident beam with a sufficient S/N ratio.

The light scattering from PVA gel was observed on polaroid film, using a He-Ne laser (GLG5260, NEC Co., Tokyo, Japan).

Turbidity Time

PVA solution with a higher degree of saponification of PVA becomes turbid with the lapse of time, and forms gel almost at the same time. The turbidity is attributed to the diffuse reflection of visible light. In order to examine the turbidity variation, the apparent absorbance at the wavelength of 700 nm was observed with the spectrophotometer (UV200S, Shimadzu Co. Ltd., Japan) as a function of time, where the turbidity time is defined as the time lapse from the solution preparation to the indication of the light absorbance at the wavelength of 700 nm (the time required for the solution becoming turbid).

Gelation Time

Gel can be defined by its infinity with regard to the weight-average molecular weight statistically or with regard to the viscosity thermodynamically. In order to examine gelation time, the viscosity of PVA solution was monitored by a falling-sphere viscometer, where the gelation time was estimated by the extrapolation of the inverse viscosity ($1/\eta$) vs. time plot to time zero.

RESULTS AND DISCUSSION

Fig.1 summarizes the observed state of PVA solutions in DMSO/water by the naked eye with varying the PVA and DMSO composition after 4 days from the preparation of those solutions at 23 °C. In this system, the turbid gel formation was observed in the mixed solvent of the composition range from 40 to 80 wt.% DMSO over 2 wt.% PVA. The gel with less turbidity was formed in the mixed solvent of the composition range from 20 to 30 wt.% DMSO over 2 wt.% PVA. 1 wt.% PVA solutions became clouded in the mixed solvent of the composition range from 40 to 80 wt.% DMSO, but formed no gel. The 1 wt.% PVA

solution seems to take further time to reach to the cross-linking density required for gelation. Below 20 wt.% DMSO and beyond 80 wt.% DMSO composition, the PVA/DMSO/water system formed no gel and maintained transparency irrespective of PVA concentration. Three patterns were found to occur in this system by varying PVA and DMSO compositions; i.e., (i) turbid gel, (ii) turbid solution, and (iii) transparent solution. DMSO concentration was an essential factor to determine turbidity and gelation in more than 2 wt.% PVA solutions.

Gelation time and turbidity time of PVA solution were estimated for various DMSO compositions. Fig.2 shows the competition between gelation and turbidity in 5 wt.% PVA solutions with varying DMSO compositions. Gelation and turbidity took place simultaneously and faster in the mixed solvent of 60 to 70 wt.% DMSO compositions in comparison with the solutions of other DMSO compositions. Below 60-70 wt.% DMSO the solution formed transparent gel at first and then became turbid, while beyond this DMSO composition the solution became turbid prior to gelation. The gelation rate and the turbidity rate were reversed at the boundary composition of 60-70 wt.% DMSO.

DMSO %\PVA %	0	10	20	30	40	50	60	70	80	90	100
1							clouded				
2											
3	trans-parent		gel				gel			trans-parent	
4											
5											

Fig. 1 Phase aspect of PVA solutions in DMSO/water with varying concentrations of PVA and DMSO.
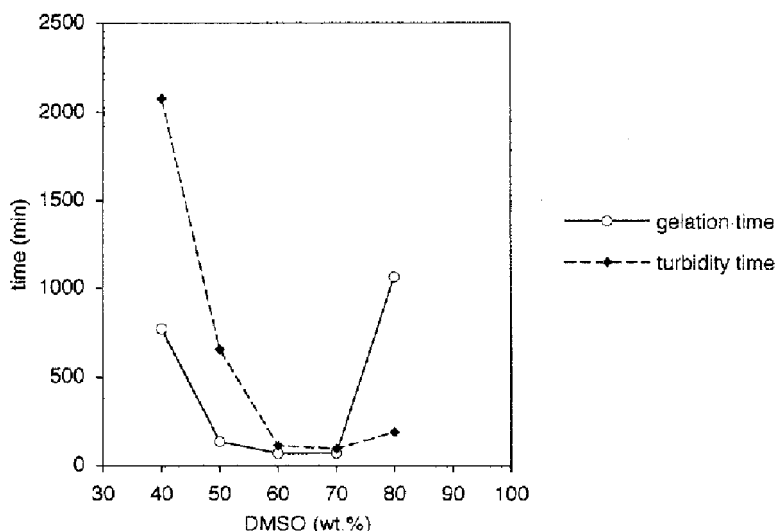

Fig. 2 Gelation and turbidity time in 5 wt.% PVA solutions with varying DMSO compositions.

Viscometry[5-8], NMR[9], and neutron scattering[10] confirm that the DMSO/water system forms a hydrated compound $(CH_3)_2SO \cdot 2H_2O$ or $(CH_3)_2SO \cdot 3H_2O$, and excess DMSO or water not incorporated in hydrated DMSO compound exists as free-DMSO or free-water, respectively. It is also suggested that free-water increases with decreasing DMSO concentration from 60-70 wt.% DMSO (corresponding to the mole ratio 2.9-2.5 of water to DMSO), while free-DMSO increases with increasing DMSO concentration from 60-70 wt.%. That is, DMSO/water solvent with 60-70 wt.% DMSO contains almost no free-water nor free-DMSO. Therefore, the gelation or turbidity is considered to be delayed by free-water or free-DMSO, where the time required for gelation and/or turbidity becomes longer in the PVA/DMSO/water system with below or beyond 60-70 wt.% DMSO.

In order to examine the competition between gelation and turbidity from the view point of PVA chain conformation, the morphology of PVA in solution was observed with various DMSO compositions by means of light scattering (LS). Fig.3(a) displays the Hv light scattering pattern observed from the 5 wt.% PVA solution in mixed solvent of 60 wt.% DMSO composition after 3 hours from solution preparation. The PVA solutions in mixed solvent of 70 or 80 wt.% DMSO composition also showed a similar LS pattern to Fig.3(a). Here the LS pattern consists of 4 wide lobes forming a four-leaf clover at 45° from the polarization direction of an incident laser beam, which is attributed to fibril crystals. Fig.3(b) shows the LS pattern from the 5 wt.% PVA solution in mixed solvent of 50 wt.% DMSO composition, and a similar pattern was also observed in mixed solvent of 40 wt.% DMSO composition. The LS pattern in Fig.3(b) consists of 4 narrow lobes forming a letter "x", attributed to small crystals. The LS pattern from the solutions containing 40-50 wt.% DMSO has grown to 4 wide lobes with the lapse of time as shown in Fig.3(a). The reason is considered as follows; the PVA/DMSO/water system with less than 60-70 wt.% DMSO composition (water-rich) forms small crystals at first, and then the crystals grow to fibrils with the lapse of time. On the other hand, the solutions in mixed solvent of 60-70 wt.% or more DMSO composition (DMSO-rich) form fibril crystals at the initial state. The PVA/DMSO/water system with 10 wt.% DMSO composition was confirmed to show narrow lobes pattern attributed to small crystals and no change to wide lobes with the lapse of time. Thus, PVA in DMSO/water solvent seems to form small crystals in water-rich solvent and fibril crystals in DMSO-rich solvent at the early stage from solution preparation.
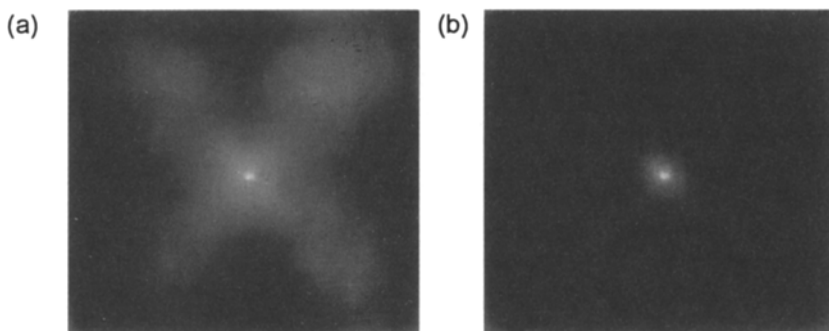
(a)   (b)

Fig. 3 Hv light scattering pattern from 5 wt.% PVA solution in mixed solvent of (a); 60 wt.% and (b); 50 wt.% DMSO compositions.

DMSO composition (wt.%)		20	40	50	60	80
just after preparation	2θ (deg.)	10.2	9.9	9.6	9.4	9.7
	B.D. (Å)	4.00	4.12	4.25	4.34	4.20
after 96 hours	2θ (deg.)	9.7	9.3	9.3	9.3	9.4
	B.D. (Å)	4.20	4.39	4.39	4.39	4.34

Table 1 Scattering angle (2θ) and corresponding Bragg distance (B.D.) at maximum scattering peak from 5 wt% PVA solution with varying DMSO composition.

Table 1 summaries the scattering angle and Bragg distance estimated from the maximum scattering peak position of PVA in DMSO/water solvent just after preparation and after 96 hours by means of wide angle X-ray scattering (WAXS) using Mokα incident beam (λ=0.71Å). As seen from Table 1, the scattering angle at the maximum peak was found to decrease eventually to the constant angle (9.3°) corresponding to the diffraction peak from (101) or (10T) of PVA crystal in all PVA solutions, where the solution in the mixed solvent of 60 wt.% DMSO composition shows the peak at 9.4° just after solution preparation. The crystallization rate of PVA in DMSO/water solvent of 60 wt.% DMSO is therefore faster than that with other DMSO compositions. Here the Bragg distance corresponding to the peak scattering angle is shorter than 4.39 Å (the (101) or (10T) space distance) at the initial stage. Since the shorter distance 4.00 Å corresponds to the interchain distance of hydrogen-bonded PVA chains the crystal nucleus is considered to be constituted by interchain hydrogen-bonding, and the PVA chains rearrange to form stable crystals with the lapse of time. The Bragg distance becomes longer to 4.39 Å in due course of crystal formation. The situation can be observed by comparing X-ray diffraction pattern taken just after solution preparation with that taken after aging for 96 hours (see Fig.4). Here the excess scattering from PVA (the scattering intensity from PVA solution or gel subtracted that from solvent) exhibits at the early stage the broad peak due to PVA interchain hydrogen-bonding, which shift its position to a smaller angle and becomes sharper according to crystal formation by aging. PVA solution containing lower (water-rich) or higher (DMSO-rich) DMSO composition than 60 wt.% shows slower crystallization rate because free-water or free-DMSO is considered to prevent PVA chains from forming interchain hydrogen bonds.

The results in this study indicate the following scheme of crystallization and subsequent gelation. PVA forms crystals in DMSO/water solvent with 20 to 80 wt.% DMSO composition, where the crystallization rate depends on DMSO composition. The crystallization rate increases with increasing DMSO composition up to 60 wt.% and decreases with further increasing DMSO composition beyond 60 wt.%. It is reported[6-10] that the mixture of DMSO and water forms a complex with the mole ratio of DMSO:water = 1:2 or 1:3. The DMSO compositions of 60 wt.% and 70 wt.% in this study correspond to the mole ratio 2.9 and 2.5 of water to DMSO, respectively, which fit to the intermediate of the reported mole ratio for DMSO/water complex. Therefore, DMSO/water solvent is considered to consist of (i) DMSO-water complex and free-water below 60-70 wt.% DMSO, (ii) DMSO-water complex with 60-70 wt.% DMSO, or (iii) DMSO-water complex and free-DMSO beyond 60-70 wt.% DMSO[11]. PVA solution in DMSO/water of 60-70 wt.% DMSO composition shows a faster crystallization

rate without being hindered by free-water or free-DMSO. Below and beyond 60-70 wt.% of the boundary DMSO composition, PVA chains will be solvated by free-water or free-DMSO molecules, and be prevented to form interchain hydrogen bonds.

PVA gelation takes place with crystallization where crystallites constitute cross-linking points. Gel is considered to be formed when the density of cross-linking points exceeds a critical amount necessary for gelation. Kanaya et al.[12] confirmed that the cross-linking points of PVA gels are composed of crystallites using wide angle neutron scattering techniques. Thus, the gelation rate is faster in the PVA/DMSO/water system with 60-70 wt.% DMSO composition due to the faster crystallization rate as seen from Fig.2. Below and beyond the boundary DMSO composition of 60-70 wt.%, gelation will be delayed by slower crystallization rate.

The priority of gelation or turbidity is considered as follows. The turbidity in the PVA/DMSO/water system is attributed to the micro-phase separation induced by the domain formation of crystalline region during crystallization[3]. Fig.3(b) indicates that small crystals are formed in the water-rich system, and the crystal domain is considered to remain small even at a gel point. Here no phase separation seems to take place and transparent gel is formed at the early stage unless the crystals grow to a certain size causing phase separation. That is, nucleation is considerably faster than subsequent crystal growth which might be suppressed by gel formation. Eventually crystals grow and phase separation takes place, resulting that the whole system becomes turbid.
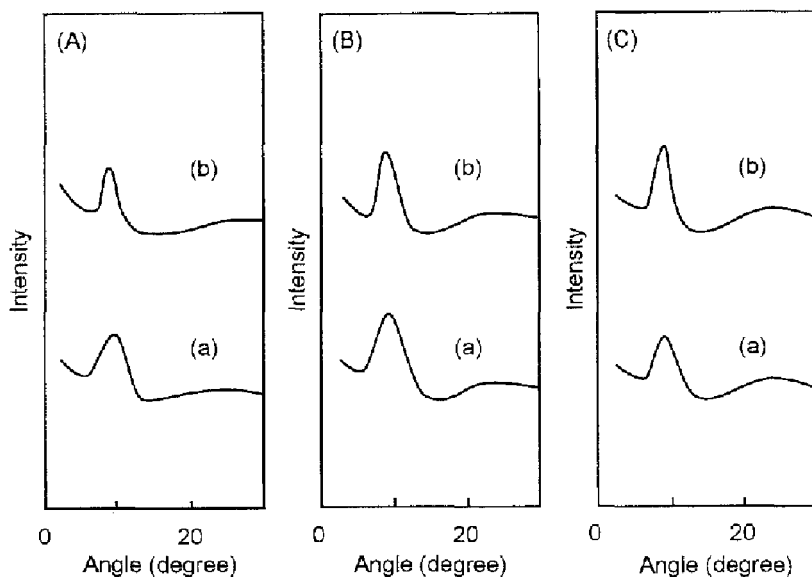

Fig. 4 Excess wide angle X-ray scattering profiles from PVA solution, (a); just after preparation and (b); after 96 hours, where DMSO compositions in solvent are (A); 40, (B); 50 and (C); 60 wt.%, respectively.

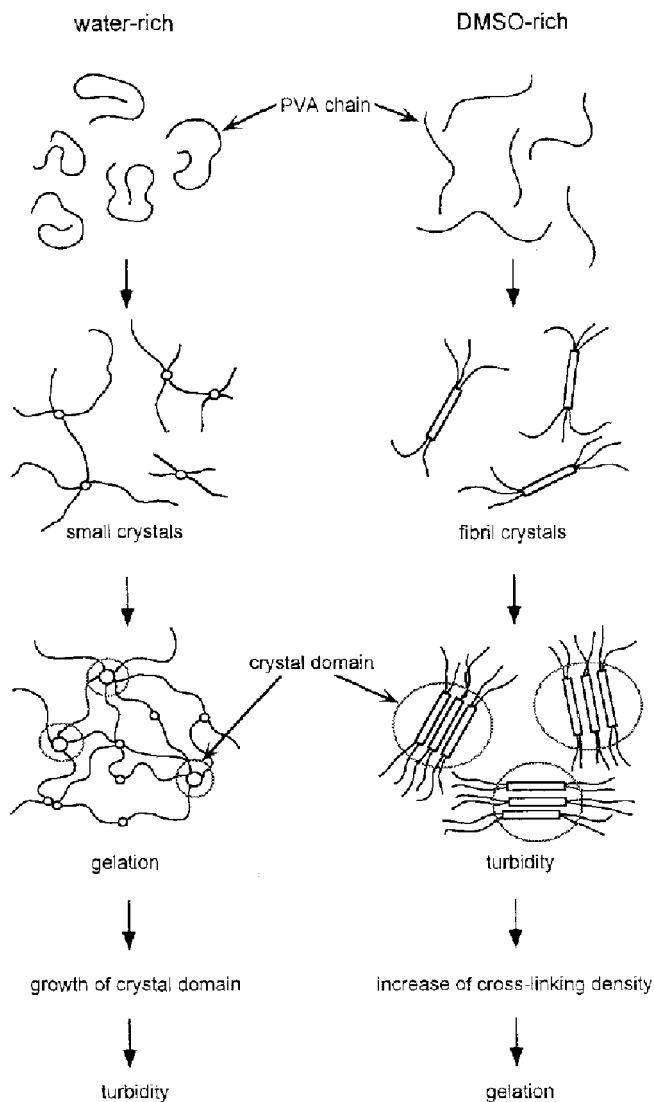water-rich   DMSO-rich

Fig. 5 Schematic illustration of PVA-gel formation in water-rich or DMSO-rich solvent.

In the DMSO-rich system (beyond 60-70 wt.% DMSO composition), PVA chain is considered to be more solvated since DMSO is a better solvent for PVA than water. Accordingly nucleation becomes slower and compatible with subsequent crystal growth. Fibril-like crystals are formed as shown from the result of light scattering (see Fig.3(a)), and induce phase

separation before enough number of crystal domains is composed for gelation. Thus, the priority of gelation or turbidity is considered to be determined by the competition between cross-linking by small crystals and crystal growth resulting in phase separation, and the boundary DMSO composition is about 60-70 wt.% in this study. The above discussion is schematically summarized in Fig.5.

CONCLUSION

PVA forms gel in DMSO/water solvent, where PVA crystallites act as cross-linking domains. Below the boundary DMSO composition of 60-70 wt.% (water-rich), transparent gel is formed at the initial stage and gel becomes turbid according to the crystal growth and subsequent phase separation, Here the nucleation is much faster than the crystal growth, so that the cross-linking density becomes high enough to form gel prior to the crystal growth to a sufficient size. Both nucleation and crystal growth are fast at the boundary DMSO composition owing that no free-water nor free-DMSO is available to prevent PVA chains from forming interchain hydrogen bonds. Here gelation and turbidity take place simultaneously in a short time.

The nucleation might be suppressed by free-DMSO above the boundary DMSO composition, and become compatible with the crystal growth. The PVA crystals grow to a sufficient size to cause micro-phase separation before the cross-linking density constituted by the crystal domains reaches to the critical point for gelation. Thus, the solution becomes turbid at first and then gelation follows by micro-phase separation.

ACKNOWLEDGMENT

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