

# Rheological Properties of Syndiotacticity-Rich Ultrahigh Molecular Weight Poly(vinyl alcohol) Dilute Solution

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**ABSTRACT:** Viscoelastic behavior of the dilute solution of ultrahigh molecular weight syndiotactic poly(vinyl alcohol) (UHMW s-PVA)/dimethyl sulfoxide (DMSO)/water was investigated through rheological response. Below a critical temperature, the dynamic storage modulus ( $G'$ ) of the solution became greater than the dynamic loss modulus ( $G''$ ) and the viscoelastic exponent for  $G'$  became smaller than that for  $G''$  before macroscopic gelation, which indicates the evolution of viscoelastic solid properties at the sol state. Also, the loss tangent ( $\tan \delta$ ) of the solution below the critical temperature increased with increasing frequency. Consequently, the dilute solution of UHMW s-PVA/DMSO/water showed the rheological behaviors as can be observed in general chemical or physical gel systems below the critical temperature. These results suggest that solid-like heterogeneity prevailed in the solution before macroscopic gelation with decreasing temperature. Such heterogeneity was considered as phase-separated domains attributed to spinodal decomposition. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 82: 569–576, 2001

**Key words:** UHMW s-PVA; gelation; rheological behavior; spinodal decomposition

## INTRODUCTION

Poly(vinyl alcohol) (PVA) is a semicrystalline polymer having hydroxyl groups that give rise to inter- and intramolecular hydrogen bondings. PVA is classified into three types, isotactic, atactic, and syndiotactic, according to the stereoregularity of the hydroxyl groups. Among them, syndiotacticity-rich PVA (s-PVA) has been known to have properties different from those of atactic PVA (a-PVA) because of the increased intermolecular hydrogen bondings between the adjacent chains. Also, molecular weight is another factor that affects the bulk and solution properties of

PVA. Recently, UHMW s-PVA of a well-oriented microfibrillar structure was synthesized<sup>1–3</sup> and its solution properties were investigated by rheological experiments, suggesting that tacticity had a significant influence on rheological properties.<sup>4,5</sup>

Most PVA solutions including PVA/water solution are well known to form thermally reversible gels at low temperature after standing several times.<sup>6–11</sup> An aqueous solution of s-PVA formed hard elastic gel more easily than did that of a-PVA and the melting point of the s-PVA gel was remarkably higher than that of a-PVA gel.<sup>12–16</sup> a-PVA hydrogels for the drug delivery system have already been reported.<sup>17–23</sup> The gelation of PVA solution was suggested to occur with or without spinodal liquid–liquid phase separation according to the concentration and temperature of

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the solution.<sup>24</sup> Test tube<sup>25,26</sup> or ball-dropping methods<sup>27</sup> have been commonly used to determine the gelation concentration and temperature of PVA solution or other polymer solutions, although these methods are lacking in providing the detailed information at the gelation threshold.

Recently, progress was achieved in elucidating the chemical<sup>28–39</sup> and physical<sup>40–44</sup> gelation behaviors, by monitoring the viscoelastic properties during the evolution of gelation. The gel point for chemically or physically crosslinked systems can be described by the following gel equation, developed by Winter and Chambon<sup>29</sup>:

$$\sigma(t) = S \int_{-\infty}^{t-t'} (t-t')^{-n} \dot{\gamma}(t') dt' \quad (1)$$

where  $\sigma$ ,  $\dot{\gamma}$ ,  $S$ , and  $n$  are the shear stress, the rate of deformation of the sample at the gel point, the gel strength parameter, and the viscoelastic relaxation exponent, respectively.  $S$  and  $n$  are the only material parameters characterizing linear viscoelastic properties. The gel point has been simply determined by the intersection of dynamic storage ( $G'$ ) and loss ( $G''$ ) moduli obtained from the oscillatory shear experiments. However, this method is valid only in the case of the stoichiometrically balanced end-linking network ( $n = \frac{1}{2}$ ).<sup>30</sup> A more general method to find the gel point is based on the fact that loss tangent ( $\tan \delta$ ) is independent of frequency at the gel point.  $G'$  and  $G''$  exhibit a power law frequency dependence at the gel point:

$$G'(\omega) \propto G''(\omega) \propto \omega^n \quad (2)$$

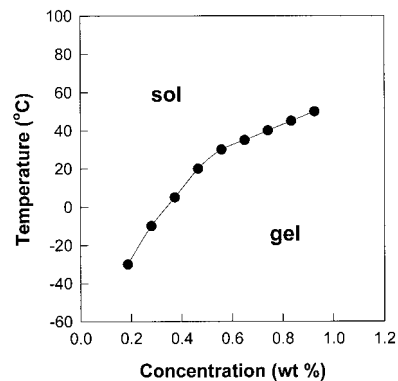
and can be described as

$$G' = G''/\tan \delta = S\omega^n \Gamma(1-n) \cos \delta \quad (3)$$

where  $\omega$  and  $\Gamma(1-n)$  are frequency and the Legendre gamma function, respectively. The phase angle ( $\delta$ ) between stress and strain is independent of frequency but proportional to  $n$ , and  $\tan \delta$  is independent of frequency at the gel point.

$$\delta = n\pi/2 \quad \text{or} \quad \tan \delta = G''/G' = \tan(n\pi/2) \quad (4)$$

In the case of PVA solution, the changes of viscoelastic characteristics induced purely by solution temperature and concentration have rarely



**Figure 1** Sol-gel diagram of UHMW s-PVA solution.

been investigated. Moreover, the information about a dilute solution of UHMW s-PVA [syndiotactic diad (s-diad) content of over 60%] is much rarer and this solution is expected to reveal interesting features in rheological experiments. The present work describes the solution properties of UHMW s-PVA/DMSO/water solution induced by temperature and concentration variations under the oscillatory shear experiments.

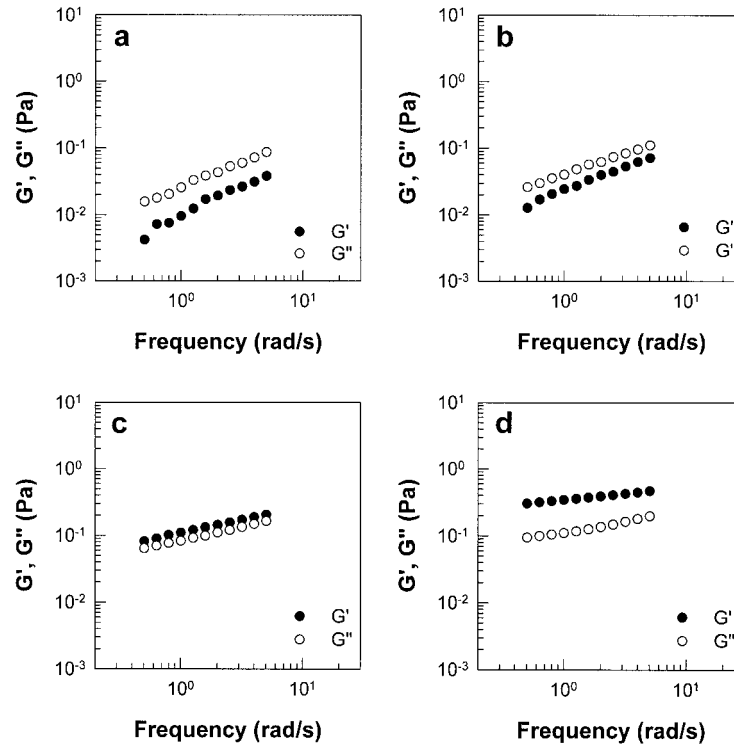
## EXPERIMENTAL

### Materials and Solution Preparation

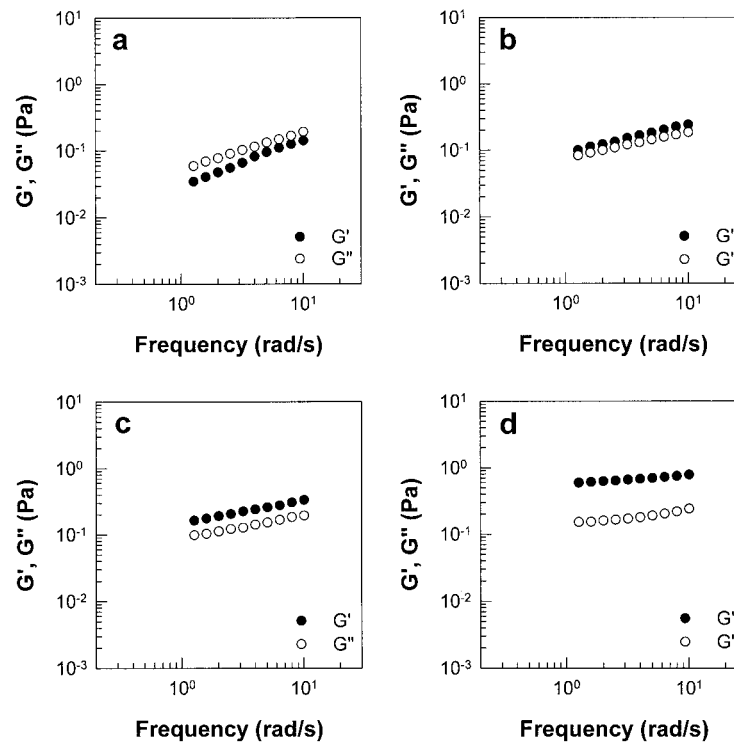
Poly(vinyl pivalate) (PVPi) was synthesized by bulk polymerization of vinyl pivalate at 30°C using 2,2'-azobis(2,4-dimethylvaleronitrile) as an initiator. UHMW s-PVA was prepared by saponifying PVPi.<sup>1–3</sup> The number-average degree of polymerization (15,500), the degree of saponification (99.9%), and the s-diad content of UHMW s-PVA (61.3%) were determined by the same method adopted in the previous study.<sup>1,2</sup> UHMW s-PVA was dissolved in a mixture of dimethyl sulfoxide (DMSO) and water (8/2 v/v) at 120°C for 2 h and was maintained for 30 min to ensure homogenization.

### Rheological Experiment

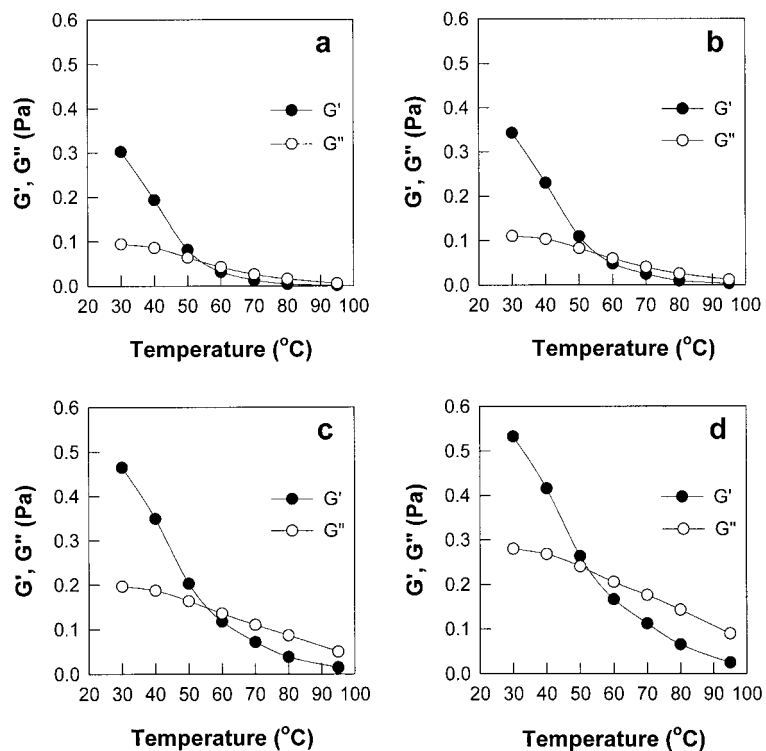
Dynamic viscoelastic properties of UHMW s-PVA solution were measured using a Rheometric Scientific ARES rheometer with a couette geometry with an outer and an inner diameter of 34 and 32 mm, respectively, at a maximum strain amplitude of 10%. The strain level was determined in the strain sweep test so that all measurements were carried out within the linear viscoelastic



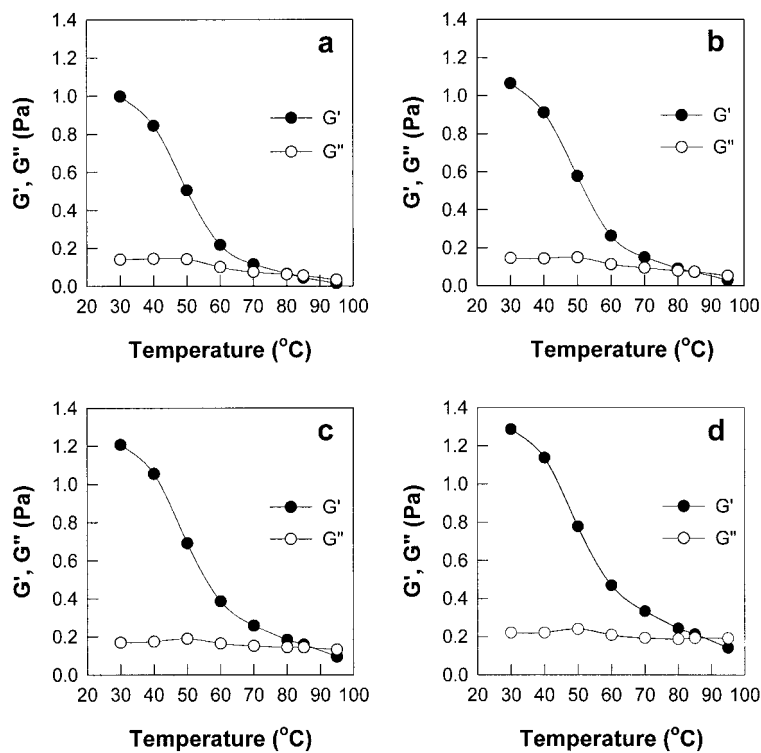
**Figure 2**  $G'$  and  $G''$  of UHMW s-PVA solution (0.2 g/dL) with frequency at different temperatures: (a) 80°C; (b) 70°C; (c) 50°C; (d) 30°C.



**Figure 3**  $G'$  and  $G''$  of UHMW s-PVA solution (0.3 g/dL) with frequency at different temperatures: (a) 95°C; (b) 80°C; (c) 70°C; (d) 50°C.



**Figure 4** Changes of  $G'$  and  $G''$  of UHMW s-PVA solution (0.2 g/dL) with temperature at different frequencies: (a) 0.5 rad/s; (b) 1.0 rad/s; (c) 5.0 rad/s; (d) 10.0 rad/s.



**Figure 5** Changes of  $G'$  and  $G''$  of UHMW s-PVA solution (0.3 g/dL) with temperature at different frequencies: (a) 0.5 rad/s; (b) 1.0 rad/s; (c) 5.0 rad/s; (d) 10.0 rad/s.

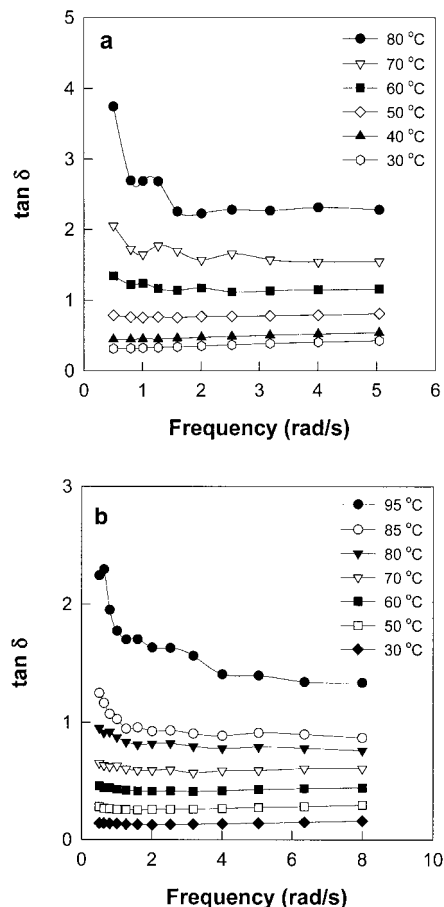
regime. Temperature was controlled from 100 to 20°C and maintained within 0.1°C of a set value.

## RESULTS AND DISCUSSION

Macroscopic gelation temperature ( $T_{\text{gel}}$ ) was measured by the test tube tilting method. Macroscopic gelation was determined to occur on the condition that the flow of solution was not observed when a test tube was tilted. The  $T_{\text{gel}}$ 's at each concentration are shown in Figure 1. UHMW s-PVA solutions with concentrations of 0.2 and 0.3 g/dL were at the sol state over 0°C.

In the present oscillatory shear experiment, the temperature was to be controlled from 100 to 20°C. Above the concentration of 0.4 g/dL,  $G'$  was greater than  $G''$  in the whole temperature range, implying that the solution was too concentrated. In our system, the molecular weight and syndiotacticity of polymer are relatively high, so the solution was considered to be diluted enough to successfully perform this experiment. Below 0.1 g/dL, the solution was so diluted that  $G'$  was always smaller than  $G''$ . Figures 2 and 3 show  $G'$  and  $G''$  of the 0.2 and 0.3 g/dL solutions, respectively, with frequency at different temperatures. In the case of the 0.2 g/dL solution,  $G'$  became greater than  $G''$  below 50°C. The same tendency was found below 80°C in the 0.3 g/dL solution. In the UHMW s-PVA solution, on cooling down temperature, liquid-like viscoelasticity decreased and a solid-like property evolved that accompanied a crossover between  $G'$  and  $G''$ . Such a crossover between  $G'$  and  $G''$  was usually found in gelation systems.<sup>28–44</sup>

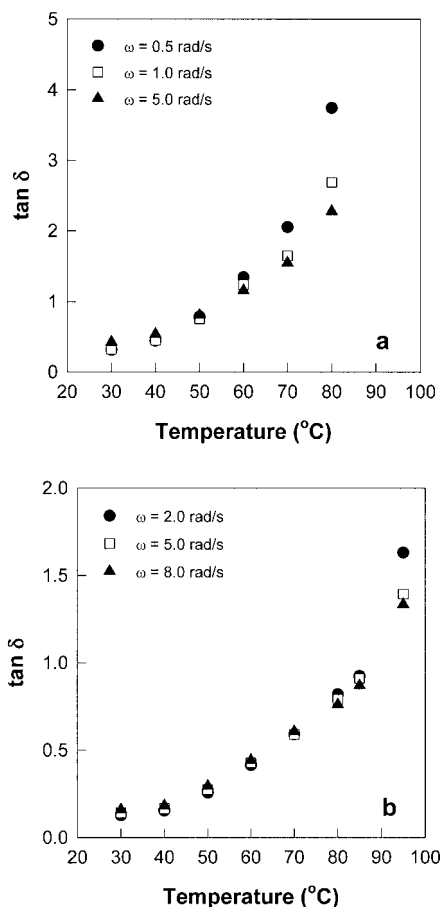
In our system, however, a noticeable point is that the crossover between  $G'$  and  $G''$  occurred at the macroscopic sol state. Moreover, the dynamic moduli of UHMW s-PVA solutions were remarkably low compared with those of a chemically crosslinked PVA system<sup>39</sup> or the other physical gelation systems.<sup>40–44</sup> This suggests that the solution did not change into the macroscopic gel state. Such behaviors, as shown in Figures 2 and 3, are clearly described from the plot of dynamic modulus as a function of temperature. Figures 4 and 5, respectively, present the changes of  $G'$  and  $G''$  of 0.2 and 0.3 g/dL solutions with temperature at different frequencies. The crossover between  $G'$  and  $G''$  was observed with decreasing solution temperature. After the crossover point,  $G'$  grew increasingly greater, indicating the significant development in the elastic property of UHMW



**Figure 6**  $\tan \delta$  of UHMW s-PVA solution with frequency at different temperatures: (a) 0.2 g/dL solution; (b) 0.3 g/dL solution.

s-PVA solution. The crossover temperature was not a constant value, although it was dependent on frequency. In the physical gelation, the crossover between  $G'$  and  $G''$  is not a definite evidence for the gel point because it is valid only in the case of the stoichiometrically balanced end-linking network. Therefore,  $\tan \delta$  and the viscoelastic relaxation exponent were considered to support the evolution of the gel-like properties at the macroscopic sol state.

Figure 6(a) shows  $\tan \delta$  of the 0.2 g/dL solution with frequency at different temperatures. Above 50°C,  $\tan \delta$  decreased with an increase in frequency, as is typical for a common viscoelastic liquid, whereas below 50°C,  $\tan \delta$  slightly increased with frequency, implying that the solution changed into the viscoelastic gel state. A constant value of  $\tan \delta$  was obtained over the frequency range at 50°C, which is a characteristic feature at the gelation threshold. As shown in



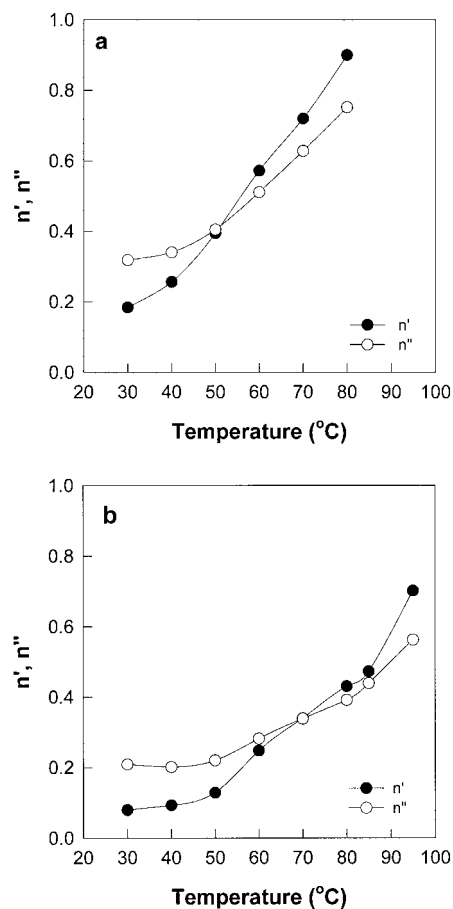
**Figure 7**  $\tan \delta$  of UHMW s-PVA solution with temperature at different frequencies: (a) 0.2 g/dL solution; (b) 0.3 g/dL solution.

Figure 6(b), a similar trend was found above and below 70°C in the case of the 0.3 g/dL solution and  $\tan \delta$  was constant and independent of frequency at 70°C.

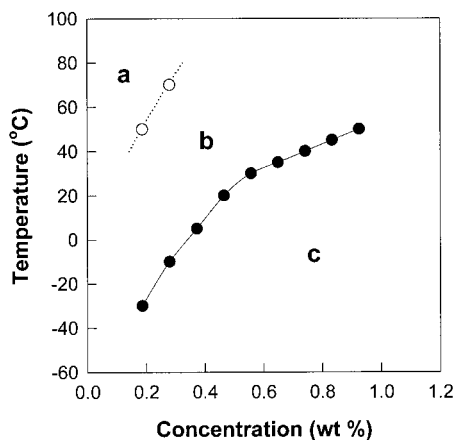
The gel point can be determined by observing a frequency-independent  $\tan \delta$  obtained from a multifrequency plot of  $\tan \delta$  as a function of temperature. From the plots in Figure 7, the frequency-independent values of  $\tan \delta$  of 0.2 and 0.3 g/dL solutions were found at 50 and 70°C, respectively. An alternative method to determine the gel point is based on the fact that the viscoelastic relaxation exponent for storage modulus ( $n'$ ) has the same value as that for loss modulus ( $n''$ ) ( $n' = n'' = n$ ).<sup>34,39,42,43</sup> The slopes of the lines of  $\log G'$  and  $\log G''$  against  $\log \omega$  yield  $n'$  and  $n''$  from eq. (2) for the frequency dependence of moduli. Figure 8(a) shows the temperature dependence of  $n'$  and  $n''$  for the 0.2 g/dL solution. Values of  $n'$  and  $n''$  decreased as temperature decreased. However,  $n'$

fell off more strongly than  $n''$ , showing that the crossover temperature between  $n'$  and  $n''$  was 50°C, which corresponds to the value obtained from Figure 7(a). As shown in Figure 8(b), the crossover of the 0.3 g/dL solution was found at 70°C, in good agreement with the result from Figure 7(b).

However, as shown in Figure 1, the macroscopic gelation did not occur in both solutions, even though the liquid-like viscoelastic properties had changed into the gel-like ones. From the results of the rheological experiment, it is obvious that the solid-like heterogeneity evolved in UHMW s-PVA solution with lowering temperature at the macroscopic sol state. The evolution of heterogeneity in the UHMW s-PVA solution is related with the formation of microstructure in the sol phase before gelation, which results from the liquid-liquid phase separation; in other words, the spinodal decomposition of PVA solution. The spinodal decomposition of PVA solution



**Figure 8**  $n'$  and  $n''$  of UHMW s-PVA solution with temperature: (a) 0.2 g/dL solution; (b) 0.3 g/dL solution.



**Figure 9** Modified sol-gel diagram of UHMW s-PVA solution.

is not a surprising phenomenon. In the light scattering study, the PVA solution had already been identified to undergo the phase separation attributed to the simultaneous process of spinodal decomposition and gelation.<sup>45-48</sup> According to results of the rheological study, the dilute solution of UHMW s-PVA is considered to undergo the transient state in the form of spinodal decomposition before macroscopic gelation. Therefore, the phase diagram of the UHMW s-PVA solution can be divided into three regions, as shown in Figure 9: (a) the homogeneous sol phase; (b) the heterogeneous sol phase displaying rheological change (i.e.,  $G' > G''$  and  $n' < n''$ ); and (c) the macroscopic gel phase, where the flow of solution no longer exists. The spinodal decomposition of the UHMW s-PVA solution was amply confirmed by rheological experiment, even though it started to occur at the relatively lower concentration and higher temperature, which is attributable to the strong intermolecular hydrogen bonding between UHMW s-PVA molecules.

## CONCLUSIONS

The rheological characterizations of the dilute solution of UHMW s-PVA/DMSO/water suggest that there exists a heterogeneous phase where some rheological properties change. In the sol state, the solution showed the rheological behaviors as can be observed in general chemical or physical gel systems below the critical temperature. UHMW s-PVA solution is considered to experience the transient state in the form of spinodal decomposition before macroscopic gelation.

Such behavior arises from the strong intermolecular hydrogen bonding and the entanglement between the long PVA chains assisting UHMW s-PVA molecules to separate themselves from the solution.

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