Phase Behavior and Physical Gelation of High Molecular Weight Syndiotactic Poly(vinyl alcohol) Solution

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Received October 2, 2000; Revised Manuscript Received January 23, 2001

ABSTRACT: The physical gelation behavior of high molecular weight (HMW) syndiotactic poly(vinyl alcohol) (S-PVA) was investigated in consideration of stereoregularity of the polymer. To precisely identify the effect of stereoregularity, syndiotactic diad (S-diad) contents of PVAs with the similar molecular weights were controlled to 61.5, 58.2, and 55.7%, respectively. The gel point (GP) of HMW S-PVA solution was determined by observing the frequency-independent loss tangent and the crossover between the relaxation exponents from the oscillatory shear experiment. The gelation process of HMW S-PVA solution with S-diad content over 58.2% was divided into two types with respect to the concentration of solution. The first type is the gelation that took place directly from sol to gel with a clear GP which was well coincident with the macroscopic gelation temperature (T_{gel}). This is for the higher concentration regime. The second one is the gelation that occurred gradually accompanying the evolution of gel-like properties in sol state without a definite GP, which is for the lower concentration regime. The gel-like heterogeneity formed during the second type gelation might be related with the liquid−liquid phase separation. In contrast, HMW S-PVA solution with S-diad content of 55.7% followed only the first type gelation. The relaxation exponent of HMW S-PVA solution at GP decreased with concentration and had a lower value than the percolation value, 0.7. The higher fractal dimension indicates the structural compactness in the cross-linking system of HMW S-PVA. As compared with the other gelation system, lower gel stiffness was obtained, suggesting that the gelation of HMW S-PVA solution occurred without a serious crystallization.

Introduction

Poly(vinyl alcohol) (PVA) is a semicrystalline polymer having hydroxyl groups which give rise to inter- and intramolecular hydrogen bondings. PVA is classified into three types, such as isotactic, atactic, and syndiotactic ones according to the stereoregularity of hydroxyl groups. Generally, PVAs with syndiotactic diad (S-diad) contents exceeding 53−54%, which is the maximum value obtained through vinyl acetate (VAc) polymerization, are called “syndiotactic”. Syndiotactic PVA (S-PVA) has been known to have different properties compared with atactic PVA (A-PVA) due to increased intermolecular hydrogen bondings between the adjacent chains. Also, molecular weight is another factor to affect the bulk and solution properties of PVA. Actually, ultrahigh molecular weight (HMW) S-PVA fibers and films have mechanical properties superior to those of atactic ones.[1−5] Recently, the in-situ formation of HMW S-PVA fiber of a well-oriented microfibrillar structure during saponification was reported by us.[1−4] In those studies, the role of syndiotacticity was obvious. HMW S-PVAs with lower S-diad contents had shapeless morphologies, but those with S-diad content higher than 56% were fibrous and had high degrees of crystallinity and orientation.[3]

In thermoreversible gelation, a fluid solution is converted into a rigid medium of infinite viscosity, and this process can be reversed by changing temperature. Most PVA solutions like PVA/water are well-known to form thermoreversible gels by lowering temperature. The stereoregularity of PVA affects the properties of a gel. Aqueous solutions of S-PVA form hard elastic gels more easily than those of A-PVA, and the melting point of S-PVA gel is remarkably higher than those of A-PVA gels.[6,7] The number of segments participating in the junction of PVA gel increased with syndiotacticity, and they were remarkably higher than the values of A-PVAs.[8] Especially, the phase separation in S-PVA gel was favored as syndiotacticity increased.[8,9]

Test tube[10] or ball-dropping[11] methods have been commonly used in determining the sol−gel transition of polymer solution, but these methods are lacking in providing the detailed information at the gelation threshold. Recently, a progress in elucidating the chemical[12−19] and physical[20−24] gelation behaviors has been achieved by monitoring the viscoelastic properties during the evolution of gelation. The gel point (GP) has been simply determined by the intersection of dynamic storage (G') and loss (G'') moduli obtained from the

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10.1021/ma001710s CCC: $20.00

Table 1. Polymerization Conditions and Molecular Parameters of HMW S-PVA

ADMVN concn (mol/mol$_{\text{monomer}}$)	VPi mol % in feed	P_n[a]	S-diad content (%)	DS (%)
3.0×10^{-4}	100	9 900	61.5	99.9
2.0×10^{-5}	60	10 400	58.2	99.9
1.0×10^{-5}	30	10 100	55.7	99.9

[a] Number-average degree of polymerization

oscillatory shear experiments. However, this method is valid only in the case of the stoichiometrically balanced end-linking network ($n = {}^1/_2$).[12-14] A more general method to find GP is based on the fact that loss tangent (tan δ) is independent of frequency.

This study describes the physical gelation behavior of HMW S-PVA with stereoregularity of the polymer. The changes in viscoelastic properties of HMW S-PVA solution induced by temperature and concentration have rarely been investigated. Moreover, the information about a dilute or a semidilute solution of HMW S-PVA with S-diad content in the vicinity of 60% is much rarer, and this solution is expected to reveal interesting features. To verify the influence of stereoregularity, three kinds of HMW S-PVAs with different syndiotacticities and similar molecular weights were synthesized and used.

Experimental Section

Materials and Solution Preparation. Poly(vinyl pivalate) (PVPi) was synthesized by the bulk polymerization of vinyl pivalate (VPi) at 30 °C using 2,2′-azobis(2,4-dimethylvaleronitrile) (ADMVN) as an initiator. HMW S-PVA with S-diad content of 61.5% was prepared by saponifying PVPi. The number-average degree of polymerization (P_n), the degree of saponification (DS), and S-diad content of HMW S-PVA were determined by the same method adopted in the previous papers[1-4] and listed in Table 1. VPi and vinyl acetate (VAc) in different mole ratios were copolymerized in bulk at 30 °C using ADMVN to produce P(VPi/VAc) copolymers having different syndiotacticities. HMW S-PVAs with S-diad contents of 58.2 and 55.7% were prepared by saponifying copoly(VPi/VAc)s.[3] The characteristics of these HMW S-PVAs are shown in Table 1.

Mixed solvent of dimethyl sulfoxide (DMSO)/water with mixing ratio of 40−80 vol % DMSO does not freeze until −40 °C.[25] When a solution freezes, gelation is difficult to determine visually. HMW S-PVA was hard to dissolve homogeneously in pure water or a water-rich mixed solvent, so a mixture of DMSO/water with 80 vol % DMSO was chosen as a solvent. HMW S-PVA was dissolved in the solvent at 120 °C for 2 h and was kept for 30 min to ensure homogenization.

Gelation Temperature. Macroscopic gelation temperature (T_{gel}) was measured by the test tube tilting method. Before the measurement, HMW S-PVA solution was kept for 1 h at a desired temperature for stabilization. Macroscopic gelation was determined to take place completely at the temperature where the solution did not flow on tilting a test tube.

Rheological Measurement. Dynamic viscoelastic properties of HMW 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 regime. Temperature was controlled from 100 to 0 °C and maintained within 0.1 °C of a set value.

Optical Microscopy. HMW S-PVA solution around the GP was examined between a slide glass and a cover glass by an optical microscope with a magnification of ×100.

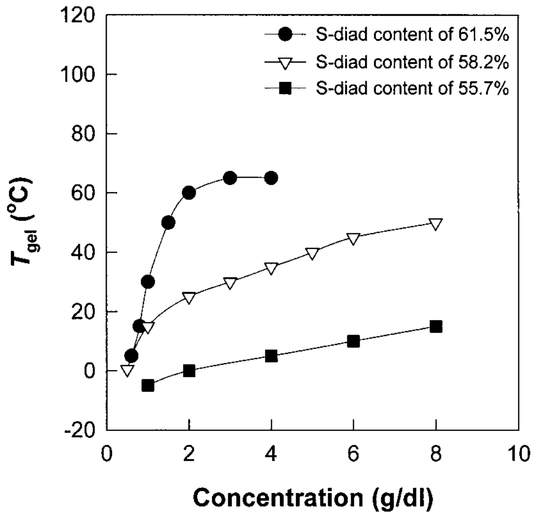

Figure 1. T_{gel} of HMW S-PVA/DMSO/water solution measured by test tube tilting method.

Results

Macroscopic Sol−Gel Transition. The macroscopic gel state is defined as the state without solution flow, and T_{gel} is thus the temperature below which a solution turns into macroscopic gel state. In this study, the dependence of time on sol−gel transition was not considered in order to avoid the complexity in interpreting the gelation behavior. Thus, the sol−gel transition was determined after the solution was kept for a fixed time, 1 h.

Determination of T_{gel} provides a sol−gel diagram as shown in Figure 1. As expected, syndiotacticity had a strong effect on gelation. The solution of HMW S-PVA with higher syndiotacticity was gelled at higher temperature and had a larger gel region in the sol−gel diagram, indicating that the gelation of HMW S-PVA solution with higher syndiotacticity is more facilitated on the condition that the molecular weight of PVA is nearly the same. This can be explained by the fact that the increase in the syndiotacticity strengthens the interaction between PVA chains by more effective intermolecular hydrogen bonds. Three kinds of samples showed commonly the concentration effect on the gelation. However, if concentration of polymer exceeds a critical concentration, a further increase of concentration had a negligible effect on T_{gel}. This is most noticeable for PVA with S-diad content of 61.5%, whose critical concentration is clearly determined to be 2 g/dL. This implies that the chain entanglement enforcing the physical gelation does not increase seriously after the solution is concentrated sufficiently. Note that “the critical concentration” is not identical among the samples, but it generally decreased with increasing syndiotacticity of PVA. This is closely related to the fact that PVA with higher S-diad content offers more effective intermolecular hydrogen bonding, giving rise to stronger physical cross-links. In general, viscosity of PVA solutions increases at the same concentration as the S-diad content of PVA increases. In reality, the 2.0 g/dL solution of HMW S-PVA with an S-diad content of 61.5% was so viscous as to be regarded as “gel-like solution”. A very weak shearing the solution between slide glasses readily produces fibrillation. However, the solutions of HMW S-PVA with 58.2 or 55.7% are not so viscous at this concentration. Thus, the properties of PVA solution,

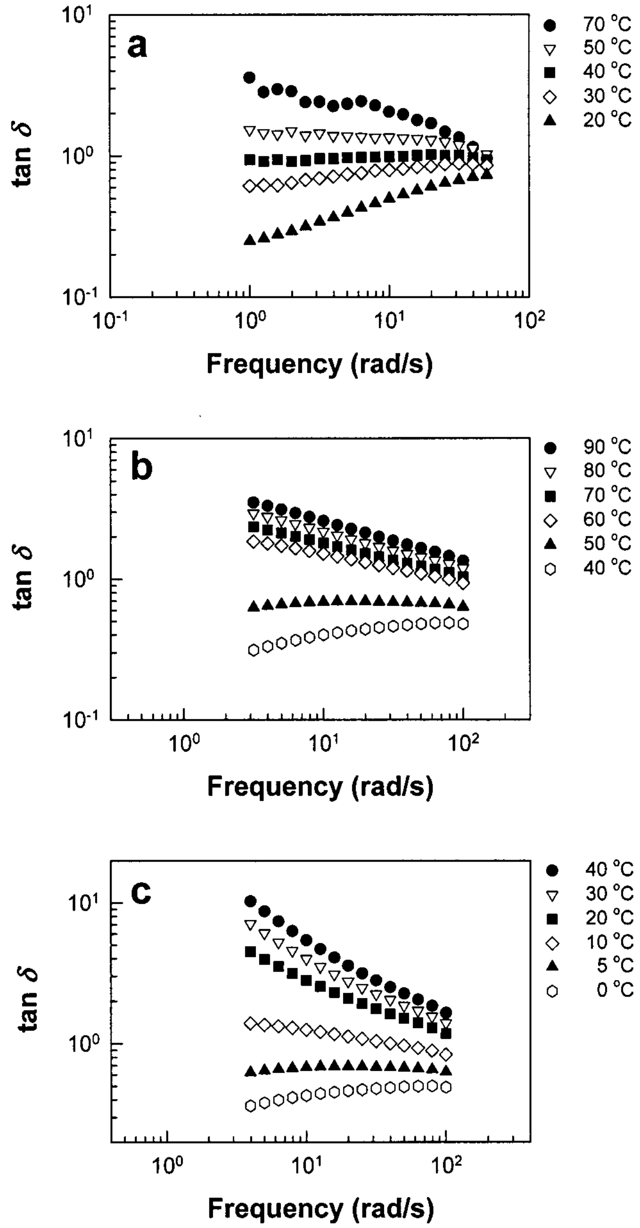

Figure 2. Loss tangent of HMW S-PVA solution with frequency: S-diad content and concentration: (a) 61.5% and 1.0 g/dL; (b) 58.2% and 8.0 g/dL; (c) 55.7% and 4.0 g/dL.

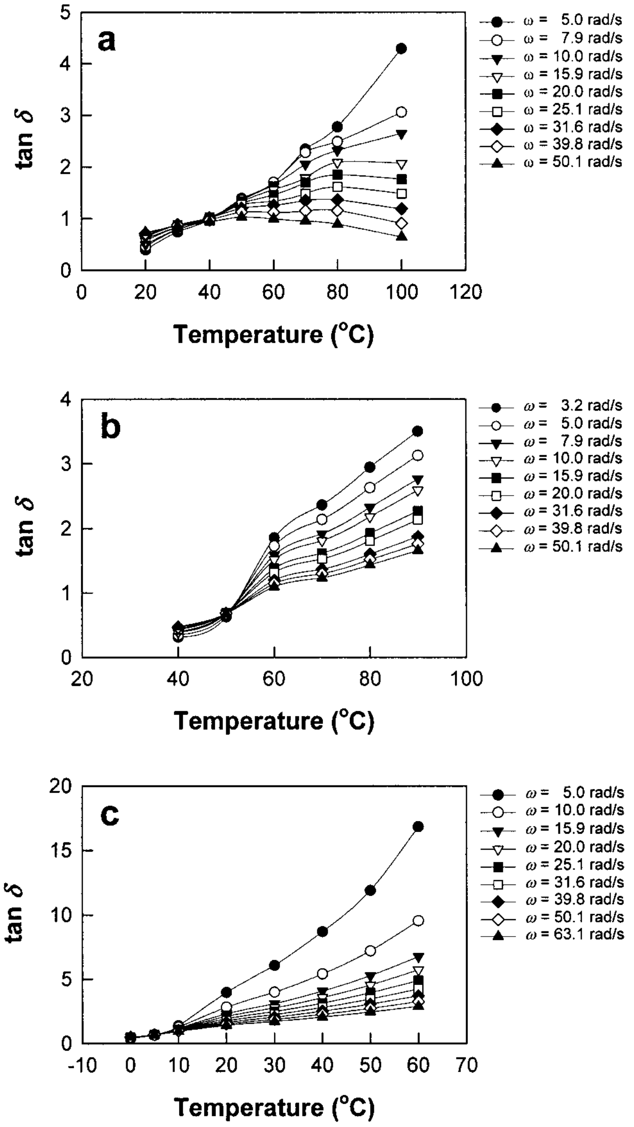

Figure 3. Multifrequency plot of loss tangent of HMW S-PVA solution with temperature: S-diad content and concentration: (a) 61.5% and 1.0 g/dL; (b) 58.2% and 8.0 g/dL; (c) 55.7% and 4.0 g/dL.

including the phase behavior, may be affected greatly by the syndiotacticity of PVA because of difference in the effectiveness of hydrogen bonding.

Rheological Behavior during Sol−Gel Transition. Consideration of tan δ provides a reliable measure for the determination of GP. A homogeneous polymer solution has the typical character of viscoelastic liquid that tan δ decreases with frequency. So, a definite decrease of tan δ with frequency denotes that a system is in a pregel regime. On the contrary, in a postgel regime, tan δ increases readily as frequency increases, indicating that the system has a viscoelastic solid property. As shown in Figure 2a, tan δ of the 1.0 g/dL solution with S-diad content of 61.5% decreased with frequency above 40 °C and increased below 40 °C, suggesting the system was a viscoelastic liquid above 40 °C and a gel below 40 °C. In addition, a frequency-independent value of tan δ was observed at 40 °C as a boundary temperature between the sol and gel phases. A similar trend was found in the 8.0 g/dL solution of HMW S-PVA with S-diad content of 58.2% (Figure 2b). The increase of tan δ below 50 °C is a typical phenomenon found in viscoelastic gel state. In Figure 2c, the frequency-independent tan δ of the 4.0 g/dL solution of HMW S-PVA with S-diad content of 55.7% was found at 5 °C.

The GP can then be determined by observing a frequency-independent tan δ obtained from a multifrequency plot of tan δ as a function of temperature. From the plots in Figure 3, the frequency-independent tan δ of 1.0, 8.0, and 4.0 g/dL solutions with S-diad content of 61.5, 58.2, and 55.7% were found at 40, 50, and 5 °C, respectively, which are well coincident with those obtained from Figure 2. Loss tangent in a whole frequency range decreased by cooling the solution due to the significant increase of G'.

The logarithmic plot of G' and G'' against frequency is shown in Figure 4. In principle, the two moduli give a crossover point at the GP on this plot.[12−14,26] That is, the GP can be defined by tan $\delta = 1$. On this background three systems may be considered to form a gel state because all the systems give the value of tan δ of

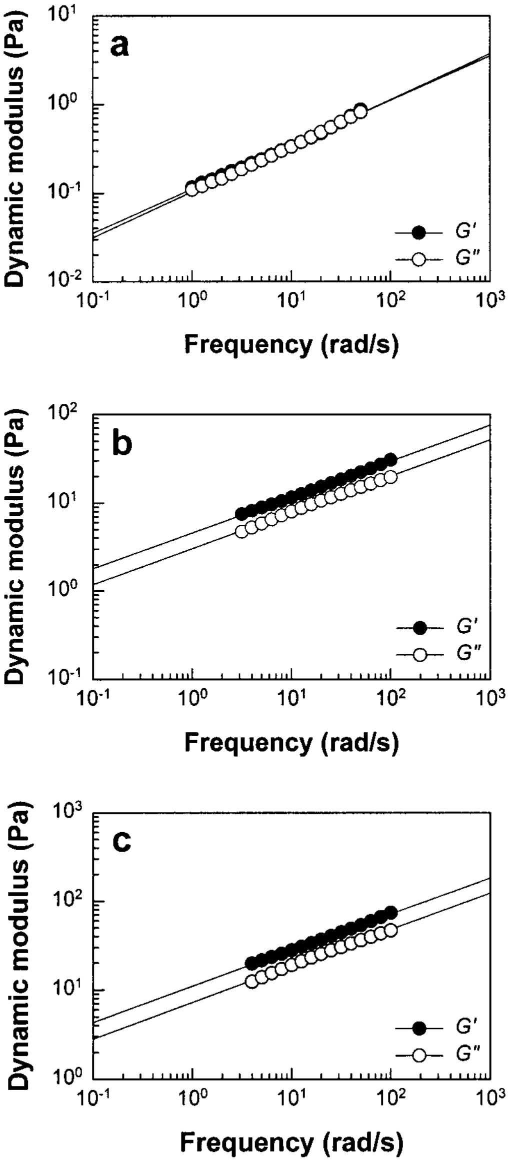

Figure 4. G' and G'' of HMW S-PVA solution with frequency at GP: S-diad content and concentration: (a) 61.5% and 1.0 g/dL; (b) 58.2% and 8.0 g/dL; (c) 55.7% and 4.0 g/dL.

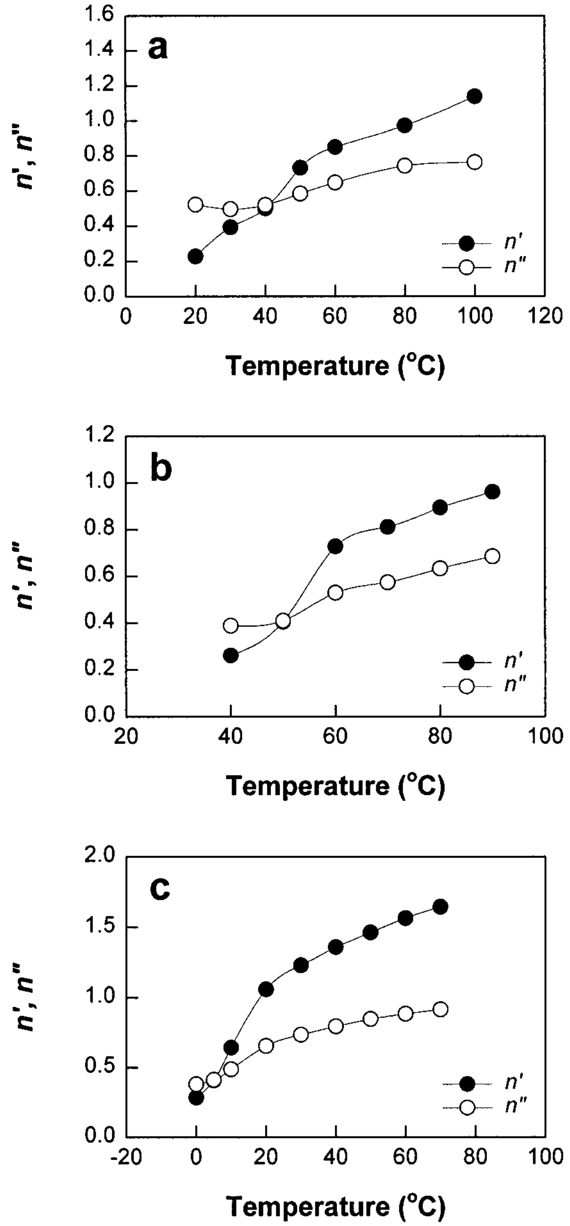

Figure 5. Change of n' and n'' of HMW S-PVA solution with temperature: S-diad content and concentration: (a) 61.5% and 1.0 g/dL; (b) 58.2% and 8.0 g/dL; (c) 55.7% and 4.0 g/dL.

approximately 1. Among the systems PVA with the highest S-diad content, 61.5%, exhibits the most clear and notable gelation.

The slopes on the logarithmic plot of G' and G'' against ω yield the viscoelastic exponent (n) for the frequency dependence of the moduli. The change of n' and n'' of HMW S-PVA solution with temperature is shown in Figure 5. As the system goes through the gelation process, the viscoelastic exponent for G' (n') falls off more seriously than the viscoelastic exponent for G'' (n''), let alone G' increases over G''. It is interesting to see that the temperature where the crossover between n' and n'' occurred is definitely coincident with the temperature where the frequency-independent tan δ was found from the multifrequency plot. From the several experimental results, the GP of HMW S-PVA/DMSO/water solution was determined, satisfying the criteria for GP. As compared with T_{gel}, the macroscopic gelation did not necessarily take place at the GP in this system. The GP was higher than T_{gel} by 10 °C in the case of the 1.0 g/dL solution of HMW S-PVA with S-diad content of 61.5%. However, the difference between GP and T_{gel} became almost negligible as the concentration of the solution increased.

The rheological behavior of HMW S-PVA solution at a more dilute concentration was investigated as well. Figure 6a shows the tan δ of the 0.6 g/dL solution of HMW S-PVA with S-diad content of 61.5%. The strong increase of tan δ in the low-frequency range appeared at 40 °C, far above T_{gel}, suggesting the evolution of the gel-like property in the macroscopic sol phase. Below 15 °C, tan δ increased in the whole frequency range, implying that the solidlike property prevailed over the system so that the macroscopic gel state was achieved. This tendency was also found in the 4.0 g/dL of the solution of HMW S-PVA with S-diad content of 58.2% (Figure 6b). In such cases as shown in Figure 6, the frequency-independent tan δ was not found, and the boundary between sol and gel was uncertain. Consequently, the determination of GP was not possibly made. Both solutions underwent three stages in the course of gelation: first, a homogeneous sol state where tan δ

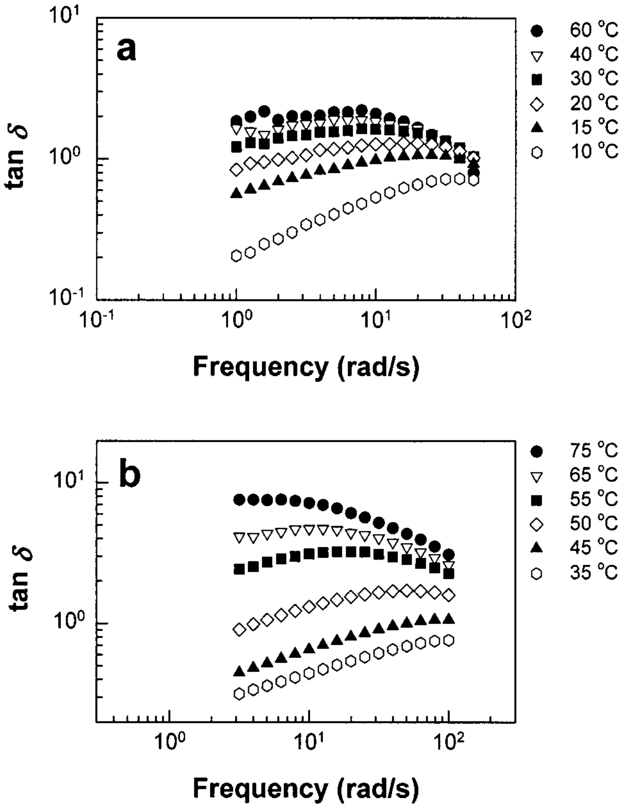

Figure 6. Loss tangent of HMW S-PVA solution with frequency: S-diad content and concentration: (a) 61.5% and 0.6 g/dL; (b) 58.2% and 4.0 g/dL.

decreased over the entire frequencies—the system was a perfect sol; second, a heterogeneous sol state where the gel-like property evolved exhibiting the increase of tan δ only in the low-frequency range; third, a perfect gel state where tan δ increased in the entire frequency range and the solution lost its fluidity. However, the concentration of HMW S-PVA solution with 58.2% was much higher than that of the solution of HMW S-PVA with 61.5%. In other words, the concentration range of HMW S-PVA solution with S-diad content of 58.2% where the gelation accompanied the evolution of the gel-like property in the macroscopic sol phase was much wider than that of HMW S-PVA solution with S-diad content of 61.5%. Unfortunately, the more dilute solution of HMW S-PVA with S-diad content of 55.7% (below 4.0 g/dL) was not investigated since the gelation occurred at too lower temperature where the rheological experiment was not performed successfully. Above 4.0 g/dL, the solution of HMW S-PVA with S-diad content of 55.7% did not display the rheological behavior as was found at the relatively low concentration of HMW S-PVA solution with S-diad content 58.2 or 61.5%.

Discussion

Phase Separation during Sol–Gel Transition. From the oscillatory shear experiment, it was evidently found that HMW S-PVA solution underwent the different gelation processes, which were divided into two types by the syndiotacticity and the solution concentration. The first type is the gelation that took place directly from sol state to gel state with a clear GP which was well coincident with T_{gel}. This type of gelation was for the solution having higher concentration and higher syndiotacticity. The second type is the gelation that occurred gradually accompanying the evolution of the gel-like properties in sol state without a definite GP. This is for the solution having lower concentration or lower syndiotacticity.

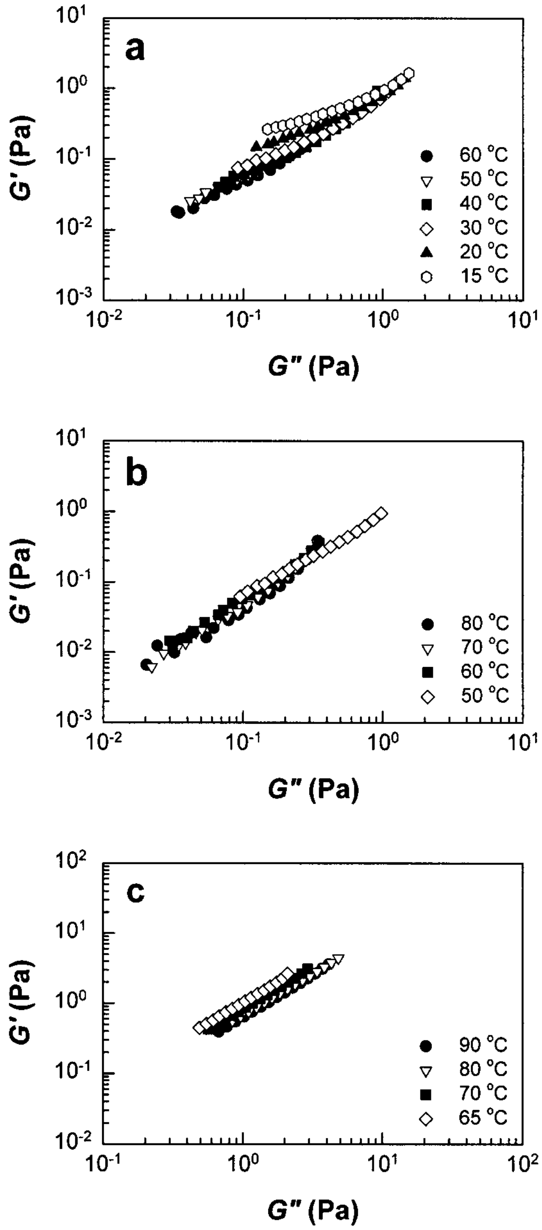

Figure 7. G' with G'' of HMW S-PVA solution with S-diad content of 61.5%. Concentration: (a) 0.6 g/dL; (b) 1.0 g/dL; (c) 4.0 g/dL.

The viscoelastic behavior of HMW S-PVA solution was closely analogous to those of the blend systems or the block copolymer systems. From the log G' vs log G'' plots of S-PVA solution with S-diad content of 61.5%, the temperature dependence was found in the 0.6 g/dL solution (Figure 7a). The similar behavior was found in 4.0 g/dL HMW S-PVA solution with S-diad content of 58.2% (Figure 8a). On the other hand, no significant temperature dependence was found in the more concentrated solutions (Figures 7b,c and 8b) and the solutions with S-diad content of 55.7% (Figure 9). Compared with the blend and block copolymer systems, the temperature dependence of the log G' vs log G'' of HMW S-PVA solution is due to a formation of microstructure in the sol phase before gelation, which may

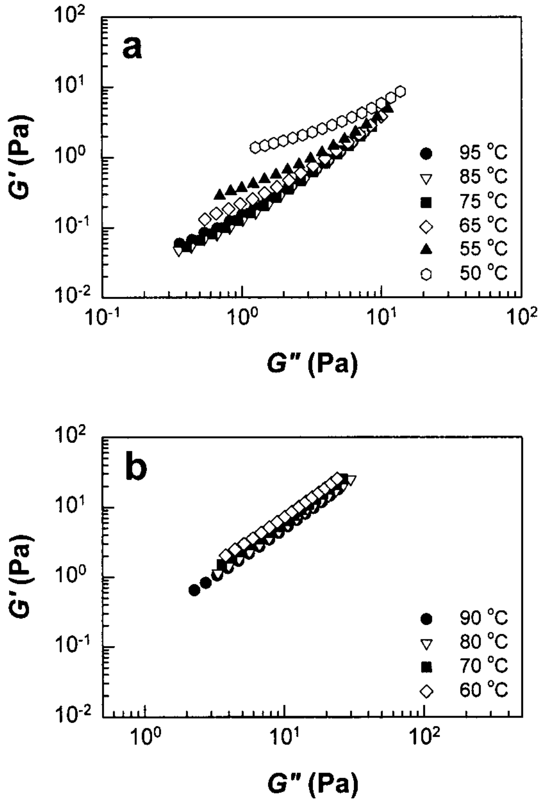

Figure 8. *G*′ with *G*″ of HMW S-PVA solution with S-diad content of 58.2%. Concentration: (a) 4.0 g/dL; (b) 8.0 g/dL.

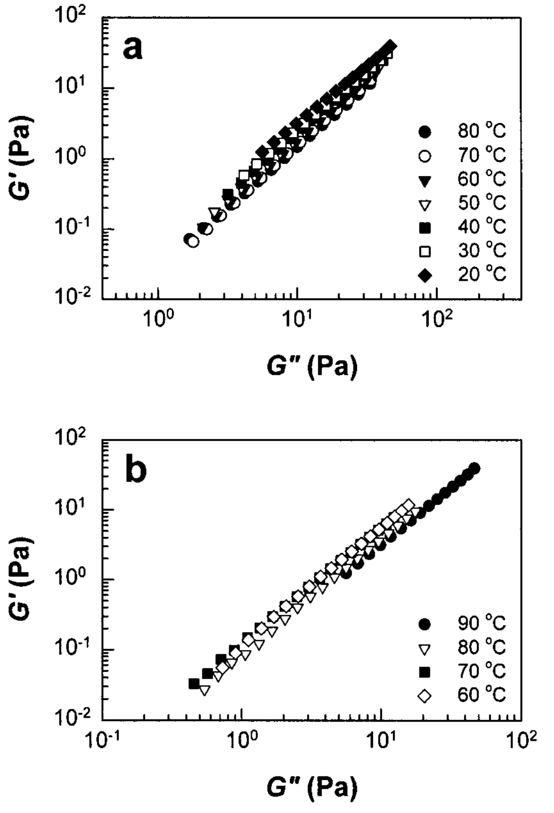

Figure 9. *G*′ with *G*″ of HMW S-PVA solution with S-diad content of 55.7%. Concentration: (a) 4.0 g/dL; (b) 8.0 g/dL.

result from the liquid–liquid phase separation, namely, the spinodal decomposition of PVA solution, giving rise to the evolution of gel-like properties mentioned in the second type of gelation.

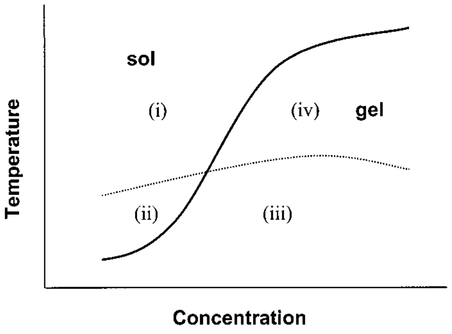

Figure 10. Phase diagram of PVA solution: sol–gel transition curve (solid line) and spinodal curve (dotted line).

The spinodal decomposition of PVA solution is not a surprising phenomenon. The light scattering study confirmed that PVA solution has an upper critical solution temperature, and the spinodal curve crosses the sol–gel transition curve.[27–29] Accordingly, the spinodal curve and the sol–gel transition curve divide the phase diagram into four regions as shown in Figure 10: the region (i) that a solution is a homogeneous sol, the region (ii) that the phase separation by spinodal decomposition takes place but a solution does not change to a gel, the region (iii) that both gelation and spinodal decomposition occur, and the region (iv) that the gelation takes place without the liquid–liquid separation. In a dilute concentration range, the solution passes through the region (ii) and finally reaches the region (iii) as temperature decreases and the solution reveals the liquid–liquid phase separation during the gelation. The second type of gelation of HMW S-PVA solution is considered to follow this procedure. Hence, the evolution of the gel-like property in the macroscopic sol state is due to the liquid–liquid phase separation. In contrast, a more concentrated solution reached the region (iii) without passing the region (ii), which represents the first type of gelation of HMW S-PVA solution.

The presence of the liquid–liquid phase separation in the gelation process of HMW S-PVA solution depends on the syndiotacticity. The 4.0 g/dL solutions are good examples to elucidate the difference in the gelation processes of HMW S-PVA solutions with different syndiotacticities. The 4.0 g/dL solution of HMW S-PVA with S-diad content of 61.5% turned from sol to gel without spinodal decomposition as shown in Figure 11a. On the other hand, the sol–gel transition curve of HMW S-PVA solution with S-diad content of 58.2% was shifted to the right side and downward as compared with that of HMW S-PVA solution with S-diad content of 61.5%. So, it should pass through the region (ii) as shown in Figure 11b. In the case of HMW S-PVA solution with S-diad content of 55.7%, the solution did not exhibit the liquid–liquid phase separation although the sol–gel transition curve of this solution was shifted to the right side and downward as compared with those of HMW S-PVA solutions with S-diad content of 61.5 and 58.2%. Matsuo et al.[29] reported the interesting result by light scattering study that, in the case of low molecular weight A-PVA/DMSO/water solution, the region (ii) is not observed and the region (iv) exists in a very narrow temperature range in the phase diagram. The spinodal curve in the phase diagram of low molecular weight A-PVA/DMSO/water solution was shifted downward as compared to that of HMW S-PVA/DMSO/water solution with S-diad content of 61.2%.[33] This is analogous to the absence of the second type of gelation of HMW S-PVA

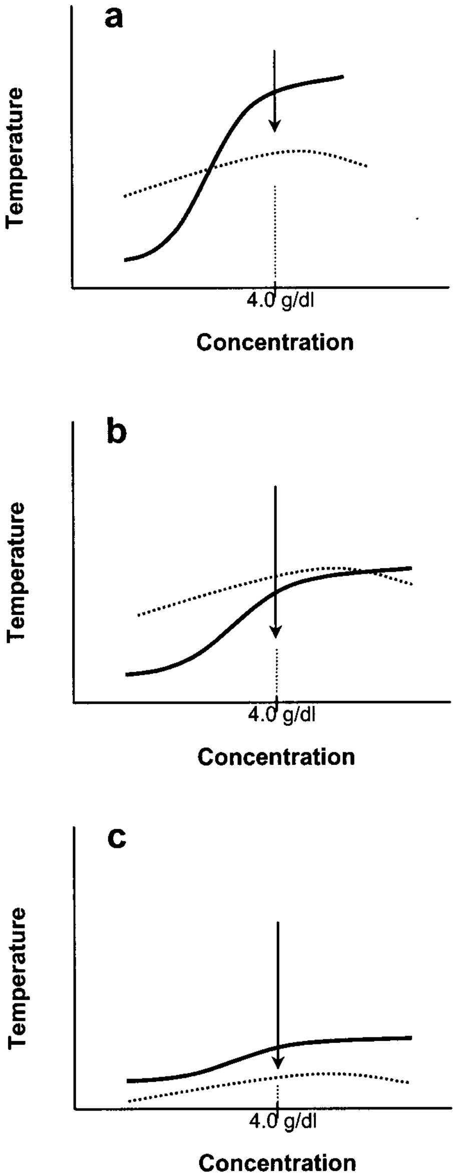

Figure 11. Illustration of sol−gel transition of 4.0 g/dL of HMW S-PVA solution having different S-diad content in the phase diagram: (a) 61.5%; (b) 58.2%; (c) 55.7%.

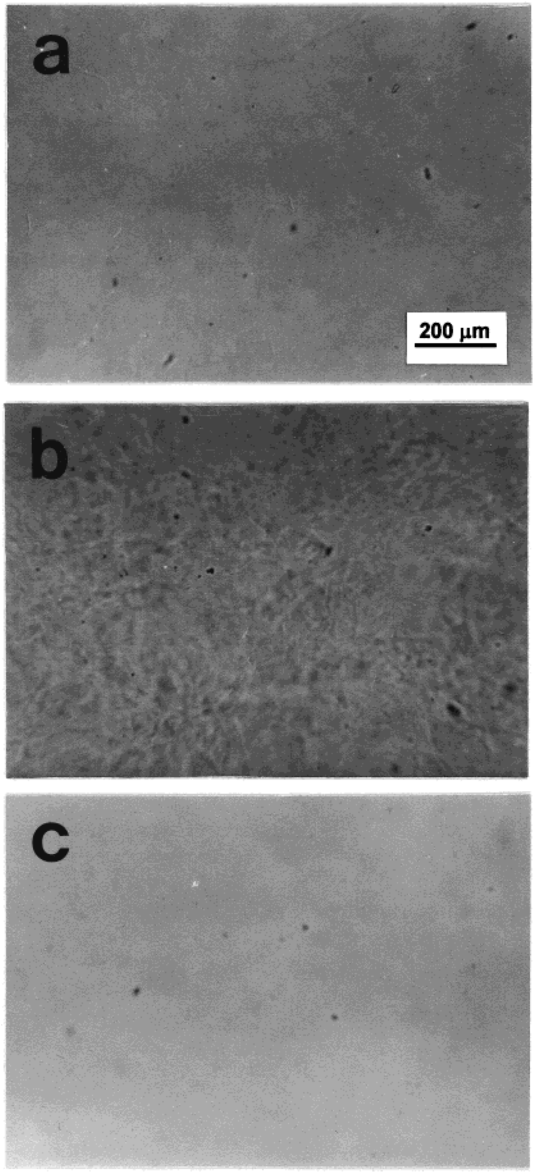

Figure 12. Optical micrograph of HMW S-PVA solutions (4.0 g/dL) at GP having different S-diad contents: (a) 61.5%; (b) 58.2%; (c) 55.7%.

Table 2. Calculated Parameters of HMW S-PVA Solution at GP

S-diad content (%)	concn (g/dL)	GP (°C)	n	FD	S (Pa·s ^{n})
61.5	1.0	40	0.51	1.99	0.09
	1.5	55	0.43	2.08	0.15
	2.0	55	0.38	2.14	0.19
	4.0	60	0.38	2.14	2.30
58.2	8.0	50	0.41	2.10	2.56
55.7	4.0	5	0.41	2.10	6.13
	8.0	15	0.41	2.10	7.97

solution with S-diad content of 55.7%. It is quite worth noting that although HMW S-PVA with S-diad content of 55.7% used in this study has a higher molecular weight and syndiotacticity than low molecular weight A-PVA, the spinodal curve is shifted downward not to show the liquid−liquid phase separation during gelation as shown in Figure 11c.

The microphotographs of 4.0 g/dL HMW S-PVA solutions at the gelation threshold are illustrated in Figure 12. The phase-separated heterogeneous appearance was exhibited in HMW S-PVA solution with S-diad content of 58.2%, while the solutions of HMW S-PVAs with S-diad contents of 61.5 and 55.7% were clear and homogeneous.

Viscoelastic Parameters at Gel Point. The viscoelastic parameters at the gelation threshold of HMW S-PVA solution, such as GP, n, fractal dimension (FD), and gel stiffness (S) are shown in Table 2. The parameters for the 0.6 g/dL solution of HMW S-PVA with S-diad content of 61.5% and the 4.0 and 6.0 g/dL solutions of HMW S-PVA solutions of S-diad content of 58.2% were not obtained because the GPs were not detectable, and the plot of log G' vs log ω did not yield a straight line, which made it impossible to obtain the power law exponent at GP. The n values at GP is about 0.4−0.5, irrespective of S-diad content of HMW S-PVA, which are lower than the percolation value, 0.7. Izuka et al.[18] investigated the molecular weight effect on n of polycaprolactone gel. They reported that n decreased with increasing molecular weight. In the present system, the molecular weight of polymer is high enough to cause the relatively lower value of n. It was indeed reported by several workers that higher solution concentration reduces *n* due to an entanglement effect.[17,19] The *n* value was reported to decrease with increasing entanglement density in entangled polymer solution system.[21] However, in nonentangled system like incipient gelatin gel, concentration rarely influences on *n*.[30] Concentration dependence was already found in chemically cross-linked PVA−glutaraldehyde gel,[19] which was identified to be “entangled”. In the present system, concentration had an effect on the *n* like the PVA−glutaraldehyde system. Especially, the value of *n* was relatively low as compared with that in the PVA−glutaraldehyde gelation. This clearly indicates that HMW S-PVA was seriously entangled owing to high molecular weight and high syndiotacticity. However, the *n* value higher than 0.4 was hard to be obtained even in the highly concentrated solution. Moreover, at higher concentration over 4.0 g/dL, syndiotacticity had little influence on the magnitude of *n*. This may be ascribable to the fact that when the concentration is sufficiently high, the entanglement reaches almost maximum to make little difference between the *n* values of HMW S-PVAs having different syndiotacticities.

G' and G'' exhibit a power law frequency dependence at GP, as shown in eq 1.

$$G'(\omega) \propto G''(\omega) \propto \omega^{n} \qquad (1)$$

and can be described as following eq 2. That is, the gel stiffness, *S*, of HMW S-PVA solution at GP was calculated from eq 2[13]

$$G' = G''/\tan\delta = S\omega''\Gamma(1 - n)\cos\delta \qquad (2)$$

where ω and $\Gamma(1 - n)$ are frequency and the Legendre gamma function, respectively. Compared with the other gelation systems, the *S* value in this system is significantly lower. This feature may rise from the fact that the gelation of HMW S-PVA solution in this study was induced by the physical process of simple cooling, whereas the other gelation systems by chemical cross-linking[18,19] or by crystallization.[22,31]

The fractal dimension, FD, is obtained from the relationship with *n* as expressed in eq 3.[32]

$$\mathrm{FD} = \frac{10n - 15}{2n - 6} \qquad (3)$$

In progress of gelation, the growth of clusters in the system can be described by FD, which is defined by $R^{\mathrm{FD}} \sim M$, where *R* is the radius of gyration and *M* is the mass of a molecular cluster, so network structure of a gel at the gel point can be represented by FD. The value of *n* has been determined theoretically by utilizing dynamic scaling, fractal analysis, and percolation of clusters. A theoretical model covering all values of *n* ($0 < n < 1$) found in various gelation systems successfully was suggested by Muthukumar.[32] In this model, it is assumed that the increase of strand length between cross-links in the incipient gel gives rise to the enhancement of the excluded-volume interaction, and the relationship between *n* and FD can be expressed by eq 3 if the excluded-volume effect is fully screened. From the calculated FD in Table 2, the concentration effect was observed. It is well-known that a critical gel with tighter network structure has a higher value of FD,[17,18,32] and FD increases with increasing polymer concentration and cross-linking density.[19] So, the higher polymer concentration of HMW S-PVA solution gives rise to the more compact structure. Compared with the PVA−glutaraldehyde system, it is particularly noteworthy that the higher value of FD was obtained, suggesting the cross-linking structure in the present gelation system is tighter than that in chemical system although the gelation occurred without cross-linkers.

Conclusions

Investigating the effect of stereoregularity on the physical gelation of HMW S-PVA solution, we may conclude as below:

The gelation process of HMW S-PVA solution was divided into two types by the concentration of solution. The first type is the gelation that took place directly from sol state to gel states with a clear GP which was well coincident with T_{gel}. This is for the concentration regime higher than the critical concentration in which T_{gel} is independent of concentration. The second type gelation occurred gradually accompanying the evolution of the gel-like property in sol state without a definite GP. This was for the lower concentration regime. The gel-like heterogeneity formed during the second type of gelation is related to the liquid−liquid phase separation. The presence of the liquid−liquid phase separation in the gelation process depends essentially on the syndiotacticity. Especially, HMW S-PVA solution having S-diad content of 55.7% had the similar gelation behavior with A-PVA solution rather than HMW S-PVA solution having S-diad content over 58%.

The relaxation exponent at GP was relatively low as compared with those of the other systems and increased with concentration, indicating the system was “highly entangled”. The higher value of fractal dimension suggests that the physically cross-linked structure in the present gelation system is very tight although the gelation occurred without cross-linkers. The significantly low gel strength was obtained in HMW S-PVA gelation system as compared with the gelation systems induced by chemical cross-linking or crystallization.

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MA001710S