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Gelation of Syndiotacticity-Rich Ultrahigh Molecular Weight Poly(vinyl alcohol) Solution

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1. INTRODUCTION

Most PVA solutions including PVA/water solution are well known to form thermally reversible gels at low temperature after standing for several times[1-6]. The gelation of PVA solution was suggested to occur with or without spinodal liquid-liquid phase separation according to the concentration and temperature of the solution[7]. Test tube[8, 9] or ball-dropping methods[10] have been commonly used in determination of the gelation concentration and temperature of PVA solution or other polymer solutions but these methods are lacking in providing the detailed information at the gelation threshold.

Recently, a progress in elucidating the chemical[11-22] and physical[23-27] gelation behaviors has been achieved by monitoring the viscoelastic properties during the evolution of gelation. 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 ($n = 1/2$)[13]. A more general method to find the gel point is based on the fact that loss tangent (tan δ) is independent of frequency at the gelation threshold.

In case of PVA solution, the changes of viscoelastic characteristics induced solely by solution temperature and concentration have rarely been investigated. Present work describes the viscoelastic behaviors of UHMW S-PVA/DMSO/water solution induced by temperature and concentration under the oscillatory shear experiments. The parameter at the gelation threshold of PVA solution was calculated and the effects of stereoregularity of PVA on the gelation behavior were discussed as well.

2. EXPERIMENTAL

2.1. Materials and Solution Preparation

2.1.1. Homopolymerization of VPi

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. UHMW S-PVA with syndiotactic diad (S-diad) content of 61.5% was prepared by saponifying PVPi.

2.1.2. Copolymerization of VPi and VAc

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. UHMW S-PVAs with S-

diad contents of 58.2 and 55.7% were prepared by saponifying copoly(VPi/VAc)s.

2.1.3. Solution preparation

UHMW S-PVA was dissolved in a mixture of DMSO and water (8/2 vol/vol) at 120 °C for 2 hours and was kept for 30 min to ensure homogenization.

2.2. 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 diameters of 34 mm 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 90 °C to 0 °C and maintained within 0.1 °C of a set value.

3. RESULTS

Macroscopic gelation temperature (T_{gel}) was measured by test tube tilting method. Macroscopic gelation was determined to occur when the flow of solution was not observed on tilting the test tube. In Figure 1, 1.0 g/dl solution of PVA with S-diad content of 61.5% showed a frequency-independent tan δ at 40°C. Above 40°C, tan δ decreased with frequency, which is typical behavior at viscoelastic sol state. In contrast, tan δ increased with frequency below 40°C, which indicates the evolution of solid-like properties at gel state. It is quite evident from the oscillatory shear experiment that 40°C is the gelation threshold (T_g) of 1.0 g/dl solution of PVA with S-diad content of 61.5%. T_g measured by rheological experiment was almost identical to T_{gel} measured by test tube tilting method or slightly higher than T_{gel}. The difference between them decreased as the concentration of PVA solution increased. On the other hand, more diluted solution (0.6 g/dl) of PVA with S-diad content of 61.5% did not have a clear frequency-independent value of tan δ and showed non-linear behavior in Figure 2. At the low frequency region, tan δ increased with frequency even at the macroscopic sol state. Such trend was favored as the concentration decreased. The similar behaviors were found in the solution of PVA with 58.2% of S-diad content in Figure 3 and Figure 4. The solution of PVA with S-diad content of 55.7% did not exhibit the non-linear behavior as shown in Figure 2 and Figure 4. The increase of tan δ in the low frequency range at the macroscopic sol state is probably due to the generation of solid-like elasticity localized in the solution. From these results, it is suggested that the stereoregularity of PVA is one of the significant factors governing the viscoelastic behaviors during gelation process.

The parameters at the gelation threshold, which should be based on the linear viscolasticity of polymer solution, were calculated in the high concentration regime and listed in Table 1. The relaxation exponent (n) at the gelation threshold were lower than the percolation value, 0.7. Izuka et al.[20] reported that n decreased with increasing molecular weight. In our system, the molecular weight of polymer is very high to cause the relatively lower value of n. It was also reported by several workers that higher solution concentration reduced n due to an entanglement effect[18, 22]. The concentration effect was also found in our system, indicating this system is "entangled". It is well known that a critical gel with more tight network

structure has a higher value of fractal dimension (*FD*) [18, 20, 28] and *FD* increases with increasing polymer concentration and crosslinker density[22]. So, the higher polymer concentration of UHMW S-PVA solution gave rise to the more compact structure of a critical gel. In the high concentration regime, *n* and *FD* was almost identical regardless of the concentration and the stereoregularity of PVA. This is mainly because the solution is sufficiently concentrated and entangled in this regime that *n* can hardly increase over the value of 0.4.

4. REFERENCES

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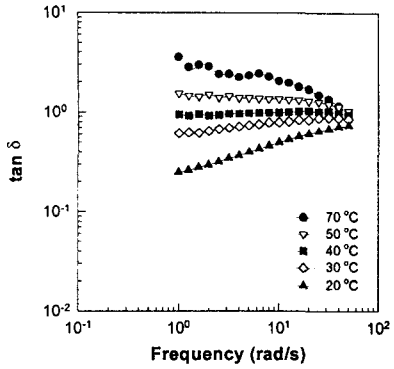

Figure 1. Loss tangent of 61.5% PVA solution (1.0 g/dl) with frequency at different temperatures.

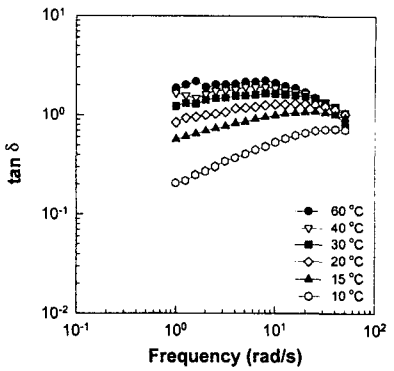

Figure 2. Loss tangent of 61.5% PVA solution (0.6 g/dl) with frequency at different temperatures

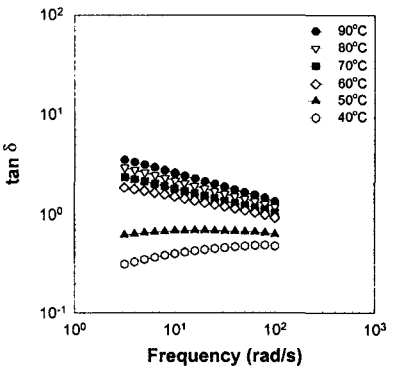

Figure 3. Loss tangent of 58.2% PVA solution (8.0 g/dl) with frequency at different temperatures.

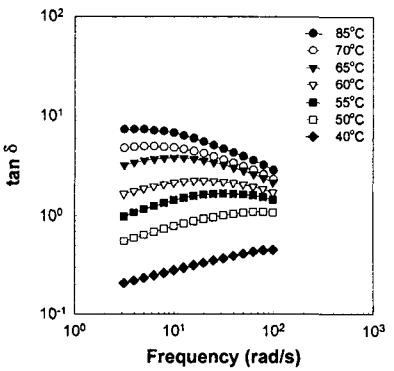

Figure 4. Loss tangent of 58.2% PVA solution (6.0 g/dl) with frequency at different temperatures

Table 1. Calculated parameters of UHMW S-PVA solution at T_g

S-diad (%)	conc. (g/dl)	T_g (°C)	n	FD	S (Pa · s)
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