Effect of stereoregularity on the properties of syndiotactic-rich ultrahigh molecular weight poly(vinyl alcohol)/dimethyl sulfoxide/water gel

Jin Hyun Choi, Won Seok Lyoo[a]*, Sohk-Won Ko**

Department of Fiber and Polymer Science, College of Engineering, Seoul National University, Seoul 151-742, Korea
sohkwonk@gong.snu.ac.kr

(Received: June 12, 1998; revised: October 12, 1998)

SUMMARY: Syndiotactic-rich ultrahigh molecular weight poly(vinyl alcohol) (UHMW S-PVA) gels having syndiotactic diad (S-diad) contents of 61.5, 58.2, and 55.7% and similar molecular weights were prepared in dimethyl sulfoxide (DMSO)/water solution. The gelation temperature of UHMW S-PVA/DMSO/water solution decreases with an increase in syndiotacticity. A great difference in the gel melting temperature (T_{gm}) was not found between the gels having an S-diad content over 58.2%. However, a significant decrease of T_{gm} was revealed in the gel having an S-diad content of 55.7%. The enthalpy of junction fusion and the number of segments participating in the junction of the UHMW S-PVA gel increases with syndiotacticity, and they are remarkably higher than the values of atactic PVAs reported in previous papers. The higher the syndiotacticity of the UHMW S-PVA gel, the higher is the dynamic storage modulus. The elasticity of the PVA gel with an S-diad content over 58.2% was recovered under cooling after heating, whereas almost no recovery was found in the gel having an S-diad content of 55.7%. The PVA gel having an S-diad content over 58.2% is opaque and exhibits a phase separated appearance in optical morphology, while the PVA gel with an S-diad content of 55.7% is almost transparent and phase separation does not occur. A highly microporous and close structure was observed for the surface of the UHMW S-PVA gels.

Introduction

Poly(vinyl alcohol) (PVA) gels are easily formed via physical pathway. Most PVA solutions, including PVA/water solution, are well known to form thermally reversible gels at low temperature, but these gels show poor mechanical properties. In order to overcome this weak point, transparent crosslinked PVA hydrogels were prepared by electron beam irradiation[1–3] or by chemical process with crosslinking agents or additives[4–8]. In spite of enhanced tensile strength and thermal resistance, such gels have low water content. On the other hand, through improved physical crosslinking processes, such as annealing[9, 10], freezing and thawing[11–13] and low temperature crystallization[14, 15] of PVA solution, PVA gels having high strength and high water content were prepared.

According to the stereoregularity of hydroxyl groups, PVA is classified into three types, i.e., isotactic, atactic, and syndiotactic ones. Among them, syndiotactic-rich PVA (S-PVA) has been known to have different properties as compared with atactic PVA (A-PVA) due to an increased intermolecular hydrogen bonding between the adjacent hydroxyl groups. Molecular weight is another factor to affect the bulk and solution properties of PVA. Actually, ultrahigh molecular weight (UHMW) S-PVA

fibers and films have superior mechanical properties to those of atactic ones[16]. Recently, UHMW S-PVA of a well-oriented microfibrillar structure was synthesized[17, 18], and its solution properties were investigated by rheological experiments, suggesting that tacticity has a significant influence on rheological properties[19]. In addition, it was found that molecular orientation during saponification is directly affected by syndiotacticity[19]. Aqueous solutions of S-PVA form hard elastic gels more easily than those of A-PVA, and the melting point of the S-PVA gel is remarkably higher than those of A-PVA gels[20–23]. Therefore, UHMW S-PVA is recommendable for the application as a gel having excellent mechanical properties without chemical crosslinking.

In this paper, in order to consider the role of syndiotacticity, UHMW S-PVAs having different stereoregularities and similar molecular weights were synthesized and UHMW S-PVA/dimethyl sulfoxide (DMSO)/water gel was prepared by quenching at low temperature. We calculated the enthalpy of junction fusion (ΔH_0) to obtain the number of segments participating in the junction (ζ) and studied the relationship between ΔH_0 or ζ and syndiotacticity. Rheological and morphological studies were carried out to investigate the effect of syndiotacticity on the characteristics of UHMW S-PVA gels.

[a]   Present address: School of Textiles, Yeungnam University, Kyongsan 712-749, Korea; wslyoo@ynucc.yeungnam.ac.kr

Experimental part

Materials and sample preparation

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. The number-average degree of polymerization (P_n), the degree of saponification (*DS*), and the S-diad content of UHMW S-PVA were determined by the same method adopted in the previous papers[17, 18] and are listed in Tab. 1.

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[24]. UHMW S-PVAs with S-diad contents of 58.2 and 55.7% were prepared by saponifying copoly(VPi/VAc)s. The characteristics of these UHMW S-PVAs are shown in Tab. 1.

Solution and gel preparation: Mixed solvent of DMSO/water with mixing ratio of 40–80 vol.-% DMSO does not freeze until −40 °C[13]. When a solution freezes, gelation is difficult to determine visually. UHMW S-PVA was hard to dissolve homogeneously in pure water and water-rich mixed solvent, so a mixture of DMSO/water with 80 vol.-% DMSO was chosen as a solvent. UHMW S-PVA was dissolved in the solvent at 120 °C for 2 h and was kept for 30 min to ensure homogenization. The homogeneous solution was quenched and kept at 0 °C for 1 day to prepare UHMW S-PVA/DMSO/water gel.

Measurements

Gelation temperature: Gelation temperature (T_{gel}) of UHMW S-PVA solution was measured by the test tube tilting method[25].

Gel melting temperature: Gel melting temperature (T_{gm}) of UHMW S-PVA gel was determined by the ball-dropping method[26]. As reported by Takahashi et al.[27], the correction by extrapolation to zero weight is negligible if the ball weight is below 100 mg. In this study, a steel ball with a diameter of 2.5 mm and a weight of 31 mg was used.

Dynamic storage modulus: Dynamic storage modulus (G') of UHMW S-PVA gel was measured using a Rheometric Scientific ARES rheometer with a couette geometry having an outer and an inner diameter of 34 mm and 32 mm, respectively, at 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 maintained within 0.1 °C of a set value. The measurement was carried out with changing temperature by 5 °C. Temperature was raised and lowered at the rate of 1 °C/min and kept for 20 min before measurement.

Turbidity: The light transmittance of UHMW S-PVA gel was measured at a wavelength of 500, 600, and 700 nm with Perkin Elmer 551S UV/VIS spectrophotometer.

Gel morphology: UHMW S-PVA gel was placed between two glass slides and examined with an optical microscope (Nikon Optipot-Pol 104). In order to be transformed into a xerogel, UHMW S-PVA gel prepared was immersed in water for 3 days for the removal of the solvent and freeze-dried at −40 °C under vacuum for 5 days. The xerogel was coated with gold, and its morphology was observed with a JEOL JSM-840A scanning electron microscope (SEM) at magnifications of 15 K and 20 K.

Results and discussion

In this study, we used UHMW S-PVAs having nearly the same P_n of 10 000 to clarify the effect of tacticity. A mixture of DMSO and water was used as a solvent for gelation, because UHMW S-PVA was difficult to dissolve homogeneously in pure water. This might be explained in our UHMW S-PVAs by the high content of syndiotactic sequences. The syndiotactic sequences in PVA play a role in the gelation, and the isotactic sequences in PVA play a role in the solubility in water. Fig. 1 shows T_{gel} of UHMW S-PVA solution in dependence of concentration. As expected, syndiotacticity has a strong effect on gelation. UHMW S-PVA having higher syndiotacticity gelled at higher temperature, indicating that the gelation of UHMW S-PVA solution with higher syndiotacticity is easier on condition that the molecular weight of PVA is nearly the same. This can be explained by the fact that the increase in syndiotacticity enlarges the interaction energy between PVA chains in the solution induced by intermolecular hydrogen bonding.

Fig. 2 shows the change of the relative ball height in UHMW S-PVA gel with temperature. T_{gm}, where the gel turned to the sol, was determined by extrapolation of the two linear portions of the graph. As shown in Fig. 3, T_{gm}'s of UHMW S-PVA gels having S-diad contents of 61.5 and 58.2% did not reveal a great difference. However, a significant decrease of T_{gm} was found in the gel of UHMW S-PVA with an S-diad content of 55.7%. From this result, it is obvious that gel melting depends on the
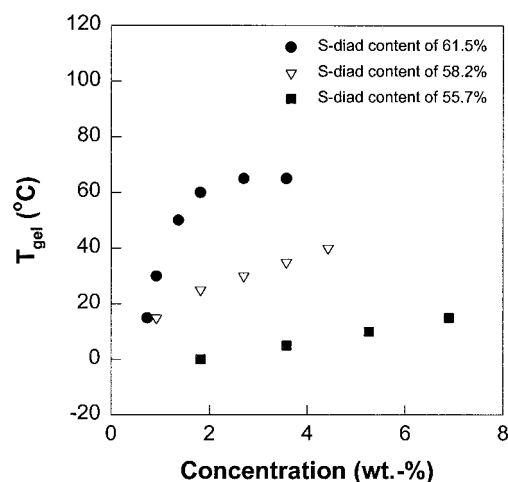

Fig. 1. Gelation temperature (T_{gel}) of UHMW S-PVA/DMSO/water solution against concentration
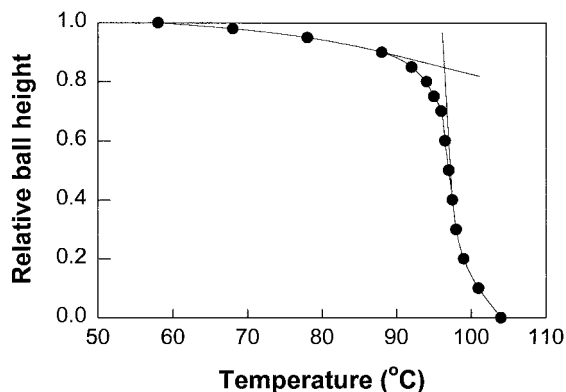
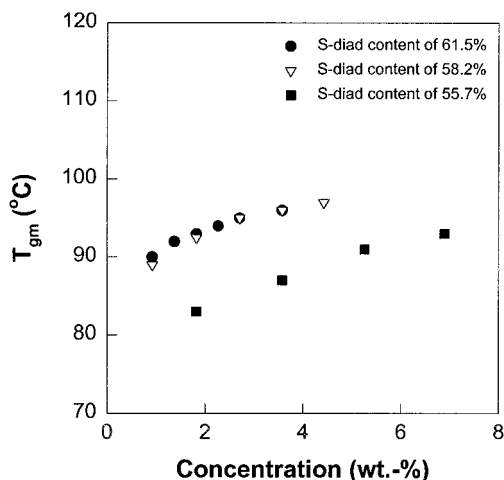Fig. 2. Change of relative ball height in 2.7 wt.-% UHMW S-PVA/DMSO/water gel having an S-diad content of 58.2%

Fig. 3. Effects of syndiotacticity and solution concentration on the melting temperature (T_{gm}) of UHMW S-PVA/DMSO/water gel

syndiotacticity of UHMW S-PVA, and the thermal resistance of PVA gel is enhanced when a highly syndiotactic PVA is used. Moreover, it is evident that the small increase in S-diad content from 55.7% to 58.2% facilitates some change in the thermal properties of UHMW S-PVA. Compared with T_{gm} of UHMW S-PVA gel, that of A-PVA gel prepared at the same concentration should be much lower.

Physical gels have complex network junctions connecting polymer chains by segmental units. The Eldridge-Ferry method[28] gives the total enthalpy of junction fusion, ΔH_0, on gel melting from the slope of $\ln c^*$ against $1/T$

$$\ln c^* = \Delta H_0/Tk_B + \text{constant} \qquad (1)$$

where c^* is the gel melting concentration, T is the absolute temperature, and k_B is the Boltzmann constant, respectively. It is known that ΔH_0 is proportional to the number of segments taking part in the junction, ζ. Tanaka et al.[29] proposed a modified Eldridge-Ferry equation as follows:

$$\ln c^* = \zeta \frac{\Delta h_0}{k_B T} - \frac{1}{s-1} \ln M + \text{constant} \qquad (2)$$

where Δh_0 is the enthalpy of bonding, s is the number of chains combined to a single junction, and M is the molecular weight, respectively. A plot of $\ln c^*$ against $10^3/T$ yields a straight line with slope $-A$ from which we can calculate ζ by Eq. (3) as

$$\zeta = \frac{10^3 k_B}{|\Delta h_0|} A = \frac{10^3 R}{|(\Delta h_0)_{mol}|} A \qquad (3)$$

where $(\Delta h_0)_{mol}$ is the enthalpy of bonding per mole of repeating unit and R is the gas constant, respectively. Fig. 4 shows the Eldridge-Ferry plot of the UHMW S-PVA/DMSO/water solutions, and the calculated values of ΔH_0 and ζ from Eq. (1) and (3) are listed in Tab. 1. In case of hydrogels of A-PVA having P_n of 1 700–17 900, a ζ value of 16.3 was obtained, which was independent of molecular weight[29]. The ζ of LMW S-PVA/water gel[30, 31] is much lower than that of UHMW S-PVA/DMSO/water gel obtained in this paper. It has been well known that a junction in PVA gel consists of syndiotactic sequences with several monomeric units corresponding to ζ. From the facts described above, it is well suggested that an individual increase in the molecular weight or the syndiotacticity does not cause a significant change of the number of syndiotactic units in a junction. As depicted in Fig. 5, in our system there is a clear dependence of ζ on syndiotacticity. Consequently, the number of syndiotactic units in a junction in the PVA gel can increase strikingly when both the syndiotacticity and the molecular weight of PVA are sufficiently high.

Fig. 6 shows the change of the dynamic storage modulus G' of UHMW S-PVA gel with temperature. A higher value of G' was obtained in UHMW S-PVA gel with higher syndiotacticity at the same temperature. This may come from the fact that the network in the UHMW S-PVA gel with a higher S-diad content is much tighter and closer. G' decreased with increasing temperature and fell off seriously as temperature approached T_{gm} owing to the local melting of the crystalline region. The slight increase of G' in Fig. 6(a) and (b) is attributed to the fact that the micro-Brownian motion of long-chain molecules between the crosslinking junctions is activated by increasing temperature, similar as in the case of A-PVA gel[32]. However, no increase of G' is found in Fig. 6(c), which is probably

Tab. 1. Characteristics of UHMW S-PVA gels

No.	P_n	S-diad content in %	DS in %	ΔH_0 kJ/mol	ζ
1	9 900	61.5	99.9	257.0	36.6
2	10 400	58.2	99.9	220.6	31.3
3	10 100	55.7	99.9	146.4	20.5
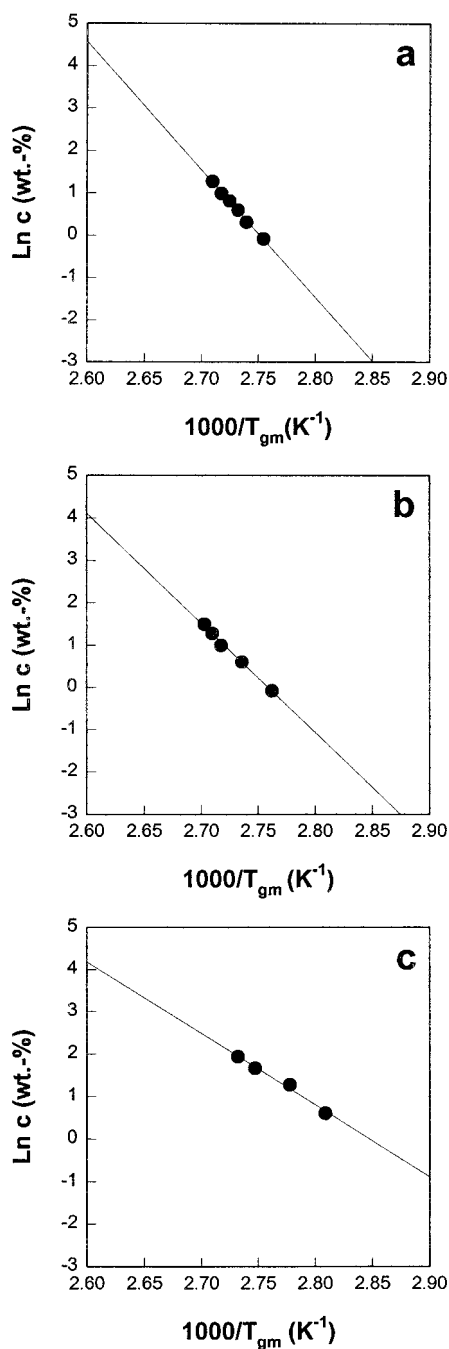
Fig. 4. Eldridge-Ferrry plot of UHMW S-PVA/DMSO/water gel: S-diad content: a, 61.5%; b, 58.2%; c, 55.7%

Fig. 5. Relation between S-diad content and ζ of UHMW S-PVA/DMSO/water gel

due to the lower T_{gm}. Partial melting occurred at lower temperature in the 55.7% UHMW S-PVA gel, so that the effect of decrease in G' was more dominant. The temperature dependence of G' of PVA gel has been discussed on the basis of the model of Nishinari et al. for thermoreversible gels[33]. There must be an upper limit for segments to be liberated from crystalline regions, because beyond this limit the chain may cease to contribute to elasticity. Relating this model with the result in Fig. 5, it is con-
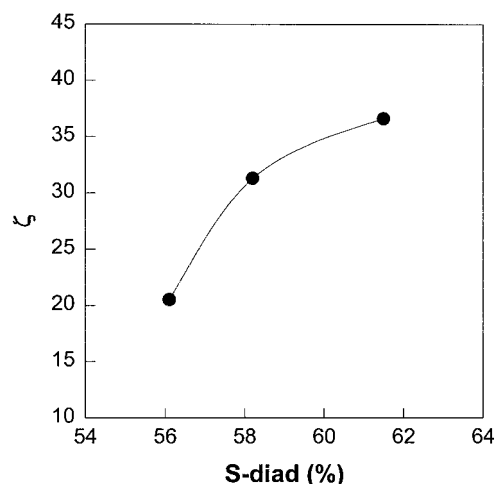
cluded that the number of segments liberated from crystalline regions as the temperature increases are fewer in UHMW S-PVA gel with higher syndiotacticity (61.5 and 58.2%) than in the 55.7% UHMW S-PVA gel. That is, the rigidity of PVA chains generated from the intermolecular hydrogen bonds is larger in UHMW S-PVA gel with higher syndiotacticity. Fig. 6 also shows the hysteresis curves of G' for the UHMW S-PVA gel. The elasticity of an agar-agar gel was recovered under cooling after heating, whereas that of A-PVA gel was not, because the hydrogen bonds once broken by heating were reproduced by cooling only in an agar-agar gel[32]. It is quite noteworthy that G' increased on recooling and that a recovery of G' of about 70% was achieved when the temperature was lowered to 25 °C in case of both 61.5% and 58.2% UHMW S-PVA gels. From the result in Fig. 6, it is clear that the crystallites responsible for the elasticity in UHMW S-PVA gel can be reconstructed easily, while those in A-PVA gel cannot. This behavior is probably due to the strong hydrogen bonding power of UHMW S-PVA molecules in a gel, which is reproducible on cooling after heating. In contrast, almost no recovery was found in the 55.7% UHMW S-PVA gel, implying that the hydrogen-bonding ability required to reform a stable gel network is relatively weak. Recovery of the elasticity of the 55.7% UHMW S-PVA gel may be achieved at the lower temperature.

Fig. 7 shows the light transmittance of UHMW S-PVA gel as a function of syndiotacticity. The influence of syndiotacticity on the turbidity is evident. The 61.5 and 58.2% UHMW S-PVA gels were opaque, while the 55.7% UHMW S-PVA gel was almost transparent. This significant decrease of transmittance of PVA gel was reported to be due to phase separation followed by crystallization[15, 25]. The turbidity of PVA gel depends on the rate of gelation and phase separation[25]. If gelation occurs
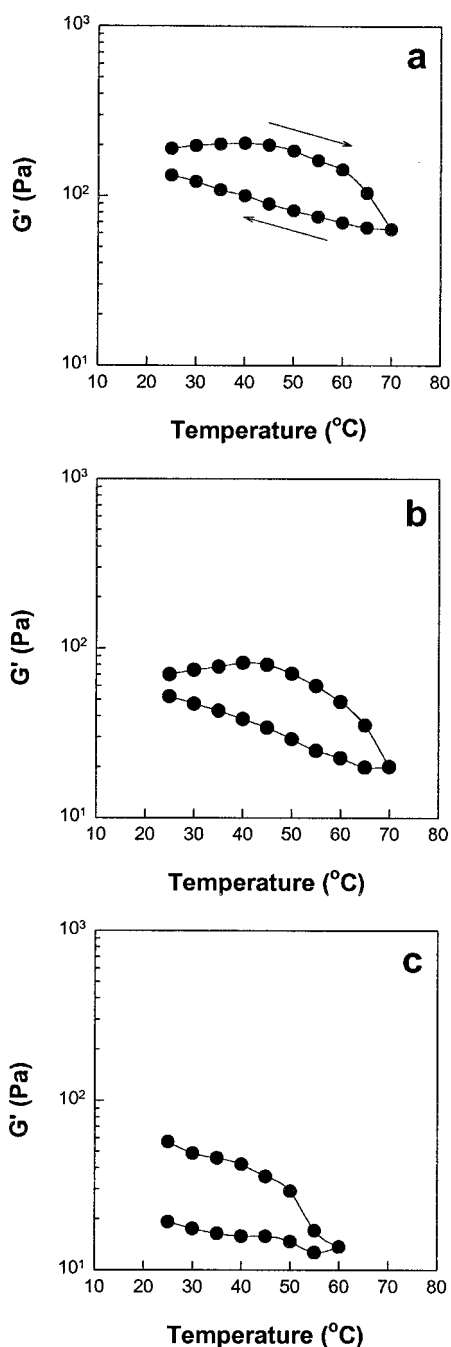
Fig. 6. Change of G' of 3.6 wt.-% UHMW S-PVA/DMSO/water gel at a frequency of 1.0 rad/s with temperature: S-diad content: a, 61.5%; b, 58.2%; c, 55.7%
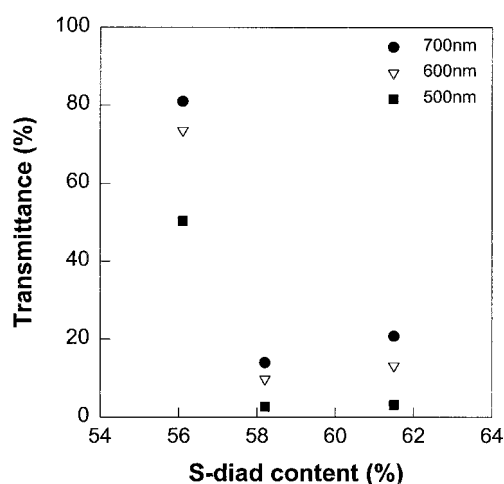

Fig. 7. Effect of syndiotacticity on the light transmittance of 3.6 wt.-% UHMW S-PVA/DMSO/water gel

UHMW S-PVA gel (Fig. 8(c)). Therefore, it is suggested that the syndiotactic configuration of the UHMW S-PVA molecule promotes phase separation, however, an S-diad content of 55.7% is not high enough to cause phase separation in the gelation process. From these results, it is identified that UHMW S-PVA solution with higher syndiotacticity favors phase separation prior to gelation. This result is coincident with those found in the in-situ fibrillation of PVA during saponification[17,18,34]. It is considered from the series of experiments that there is marked change in the characteristics and properties of UHMW S-PVA gel having an S-diad content over 58.2%. It is supported by the structural investigation of S-PVA in the previous work[24]. The structures of S-PVA showed a sharp transition between 55 and 56% S-diad content. PVA with lower S-diad content had a shapeless morphology, but at 56% S-diad content the polymer was fibrous, with higher degree of crystallinity and orientation of the crystallites.

In Fig. 9, the SEM morphology of UHMW S-PVA xerogel is illustrated. A highly microporous structure was developed on the surface of the gel. The micropores in PVA hydrogel are originated from the solvent or the solution of weak concentration phase, which is liquid-liquid phase separated in a gel[35]. The micropores should orient normal to the freezer plate in order to release the phase-separated liquid out of the gel surface, which is confirmed in Fig. 9(b), suggesting that a liquid-liquid phase separation occurred in UHMW S-PVA gel. Actually, several drops of the phase-separated liquid were observed on the surface of UHMW S-PVA gel in the progress of the gelation. The pore size of UHMW S-PVA gel was below 1 μm, much smaller than that reported in previous work[35,36], implying that the gel structure of UHMW S-PVA gel is fairly close. Considering the structure and property relationship, this close structure of UHMW S-PVA gel having fine porosity plays a significant role in enhancing T_{gm} and elasticity.
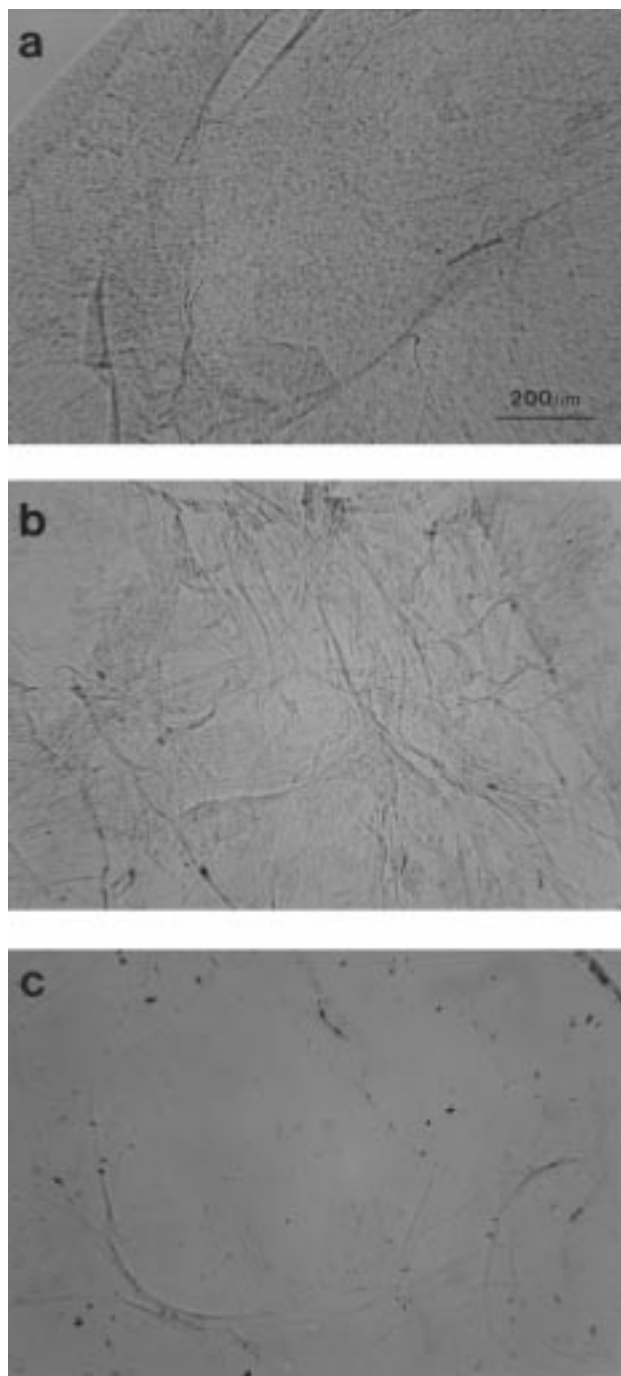
before phase separation, a homogeneous gel structure develops and phase separation is greatly inhibited. If phase separation occurs faster than gelation, the gel becomes opaque. Consequently, the significant decrease of transmittance is evidence of a phase separation accompanied by gelation of the 61.5 and 58.2% UHMW S-PVA solutions. The phase separated heterogeneous gel morphology is exhibited in Fig. 8(a) and (b). In contrast, the phase separation did not occur seriously in the 55.7%
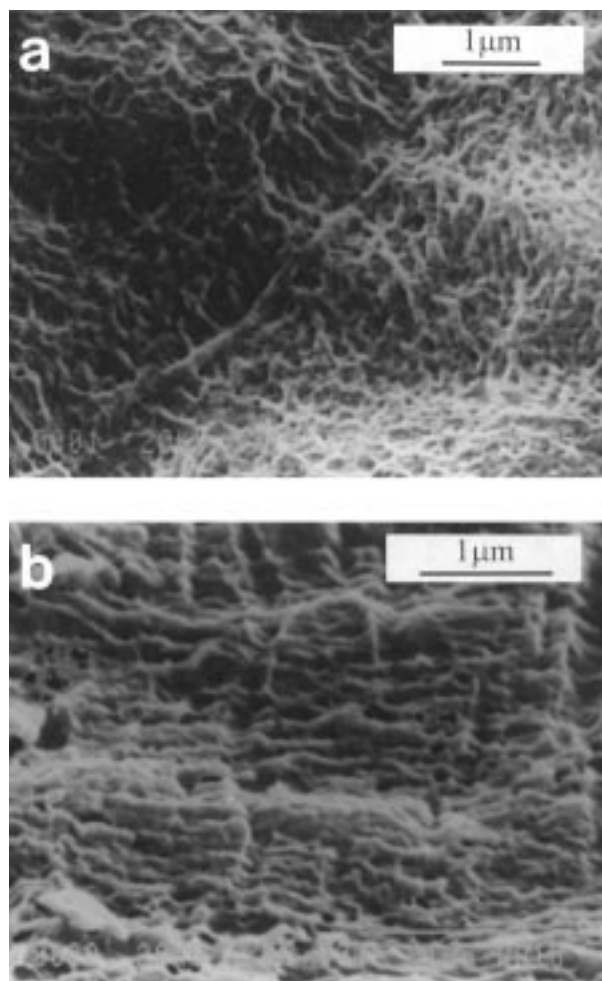
Fig. 9.   SEM micrograph of 3.6 wt.-% UHMW S-PVA/DMSO/ water xerogel having S-diad contents of 61.5%: a, normal to the surface (15 K); b, parallel to the pore orientation (20 K)

Fig. 8.   Optical micrographs of the 3.6 wt.-% UHMW S-PVA/ DMSO/water gel; S-diad content: a, 61.5%; b, 58.2%; c, 55.7% (magnification 0.1 K)

Conclusions

The syndiotacticity of PVA promotes the increase of T_{gm}, ζ, G', and turbidity of UHMW S-PVA/DMSO/water gel. ζ increases strikingly when both the syndiotacticity and the molecular weight of PVA are sufficiently high. G' of UHMW S-PVA gels having an S-diad content over 58.2% recovered to about 70% on cooling after heating, whereas

almost no recovery was found in the gel having an S-diad content of 55.7%. This is probably due to the stronger hydrogen bonding power of UHMW S-PVA molecules having an S-diad content over 58.2% which is reproducible on cooling after heating. The significant increase in turbidity of UHMW S-PVA gel with an S-diad content over 58.2% is evidence of phase separation accompanied by gelation, which is confirmed in the heterogeneous appearance. Through the series of experiments, it is considered that a profound change is found in the characteristics and properties of UHMW S-PVA gels with S-diad contents between 55.7% and 58.2%. The close structure of UHMW S-PVA gel having fine porosity may play a role in enhancing T_{gm} and elasticity. Conclusively, increasing the syndiotacticity is one of the most effective ways for enhancing the thermal and mechanical properties of PVA gel.

1) N. A. Peppas, E. W. Merrill, *J. Appl. Polym. Sci.* **14**, 441 (1976)
2) N. A. Peppas, E. W. Merrill, *J. Appl. Polym. Sci.* **21**, 1763 (1977)
3) D. Darwis, F. Yoshi, K. Makuuchi, M. T. Razzak, *J. Appl. Polym. Sci.* **55**, 1619 (1995)
4) F. Suzuki, K. Onozato, *J. Appl. Polym. Sci.* **39**, 371 (1990)
5) J. Bo, *J. Appl. Polym. Sci.* **46**, 783 (1992)
6) M. Shibayama, M. Adachi, F. Ikkai, H. Kurokawa, S. Sakurai, S. Nomura, *Macromolecules* **26**, 623 (1993)
7) Y. An, T. Koyama, K. Hanabusa, H. Shirai, J. Ikeda, H. Yoneno, T. Itoh, *Polymer* **36**, 2297 (1995)
8) Y. Zhuang, Z. Zhu, L. Chen, *J. Appl. Polym. Sci.* **63**, 267 (1997)
9) N. A. Peppas, E. W. Merrill, *J. Biomed. Mater. Res.* **11**, 423 (1977)
10) T. Tanigami, K. Murase, K. Yamaura, S. Matsuzawa, *Polymer* **35**, 2753 (1994)
11) M. Watase, K. Nishinari, *Makromol. Chem.* **189**, 871 (1988)
12) M. Nagura, T. Hamano, H. Ishikawa, *Polymer* **30**, 762 (1989)
13) K. Yamaura, M. Itoh, T. Tanigami, S. Matsuzawa, *J. Appl. Polym. Sci.* **37**, 2709 (1989)
14) S. H. Hyon, W. I. Cha, Y. Ikada, *Polym. Bull.* **22**, 119 (1989)
15) W. I. Cha, S. H. Hyon, Y. Ikada, *Makromol. Chem.* **193**, 1913 (1992)
16) K. Nakamae, Y. Nishino, H. Ohkubo, S. Matsuzawa, K. Yamaura, *Polymer* **33**, 2581 (1992)
17) W. S. Lyoo, W. S. Ha, *Polymer* **37**, 3121 (1996)
18) W. S. Lyoo, W. S. Ha, *J. Polym. Sci., Part A: Polym. Chem.* **35**, 55 (1997)
19) W. S. Lyoo, W. S. Ha, B. C. Kim, *Polym. Eng. Sci.* **37**, 1259 (1997)
20) K. Ogasawara, T. Nakajima, K. Yamaura, S. Matsuzawa, *Progr. Colloid Polym. Sci.* **58**, 145 (1975)
21) K. Ogasawara, T. Nakajima, K. Yamaura, S. Matsuzawa, *Colloid Polym. Sci.* **254**, 456 (1976)
22) K. Ogasawara, T. Nakajima, K. Yamaura, S. Matsuzawa, *Colloid Polym. Sci.* **254**, 553 (1976)
23) S. Matsuzawa, K. Yamaura, R. Maeda, K. Ogasawara, *Makromol. Chem.* **180**, 229
24) W. S. Lyoo, J. Blackwell, H. D. Ghim, *Macromolecules* **31**, 4253 (1998)
25) M. Ohkura, T. Kanaya, K. Kaji, *Polymer* **33**, 3686 (1992)
26) R. S. Jackson, D. I. Bower, W. F. Maddams, *Polymer* **31**, 857 (1990)
27) A. Takahashi, M. Sakai, T. Kato, *Polym. J.* **12**, 335 (1980)
28) J. E. Eldridge, J. D. Ferry, *J. Phys. Chem.* **58**, 992 (1954)
29) F. Tanaka, K. Nishinari, *Macromolecules* **29**, 3625 (1996)
30) K. Shibatani, *Polym. J.* **1**, 348 (1970)
31) A. Takahashi, S. Hiramitsu, *Polym. J.* **6**, 103 (1974)
32) M. Watase, K. Nishinari, *Polym. Commun.* **24**, 270 (1983)
33) K. Nishinari, S. Koide, K. Ogino, *J. Phys. (Paris)* **46**, 793 (1985)
34) W. S. Lyoo, W. S. Ha, *Polymer*, in press (1998)
35) F. Yokoyama, I. Masada, K. Shimamura, T. Ikawa, K. Monobe, *Colloid Polym. Sci.* **264**, 595 (1986)
36) H. H. Trieu, S. Qutubuddin, *Colloid Polym. Sci.* **272**, 301 (1994)