

# Effect of Stereoregularity on the Properties of Syndiotacticity-Rich Ultrahigh Molecular Weight Poly(vinyl alcohol) /Dimethylsulfoxide/Water Gel

Jin Hyun Choi, Won Seok Lyoo\*, and Sohk Won Ko

*Department of Fiber and Polymer Science, College of Engineering, Seoul National University*

*\*Electronic Materials and Devices Research Center, Korea Institute of Science and Technology*

## 1. 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 showed poor mechanical properties. In order to overcome this weak point, transparent crosslinked PVA hydrogels were prepared by electron beam irradiation<sup>1-3</sup> or by chemical process with crosslinking agents or additives<sup>4-8</sup>. In spite of enhanced tensile strength and thermal resistance, such gels have low water content. On the other hand, through the improved physical crosslinking processes, such as annealing<sup>9, 10</sup>, freezing and thawing<sup>11-13</sup> and low temperature crystallization<sup>14, 15</sup> 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, such as isotactic, atactic, and syndiotactic ones. Among them, syndiotacticity-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. Also, 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<sup>16</sup>. Recently, UHMW S-PVA of a well-oriented microfibrillar structure was synthesized<sup>17, 18</sup> and its solution properties were investigated by rheological experiments to suggest that tacticity had a significant influence on rheological properties<sup>19</sup>. In addition, it was found that molecular orientation during saponification was directly affected by syndiotacticity<sup>19</sup>. Aqueous solutions of S-PVA formed hard elastic gels more easily than those of A-PVA and the melting point of the S-PVA gel was remarkably higher than those of A-PVA gels<sup>20-23</sup>. Therefore, UHMW S-PVA is recommendable for the application as a gel having excellent mechanical properties without chemical crosslinking.

In this study, in order to consider the role of syndiotacticity, UHMW S-PVAs having different stereoregularities and similar molecular weights were synthesized and UHMW S-PVA/dimethylsulfoxide (DMSO)/water gel was prepared by quenching at low temperature. We calculated the enthalpy of junction fusion ( $\Delta H_0$ ) to obtain the number of segments participating in the junction ( $\zeta$ ) and studied the relationship between  $\Delta H_0$  or  $\zeta$  and syndiotacticity. Rheological and morphological studies were carried out to investigate the effect of syndiotacticity on the characteristics of UHMW S-PVA gels.

## 2. Experimental

### 2.1. Materials and sample preparation

#### 2.1.1. Homopolymerization of VPi

#### 2.1.2. Copolymerization of VPi and VAc<sup>24</sup>

#### 2.1.3. Solution and gel preparation

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.

### 2.2. Measurements

Gelation temperature ( $T_{gel}$ ) of UHMW S-PVA solution was measured by test tube tilting method<sup>25</sup>. Gel melting temperature ( $T_{gm}$ ) of UHMW S-PVA gel was determined by the ball-dropping method<sup>26</sup>. 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 diameters of 34 mm and 32 mm, respectively, at maximum strain amplitude of 10%. 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. The light transmittance of UHMW S-PVA gel was measured at the wavelength of 500, 600, and 700 nm with Perkin Elmer 551S UV/VIS spectrophotometer. The observation of gel morphology was carried out as following; UHMW S-PVA gel was placed between two glass slides and examined with 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  $-40\text{ }^{\circ}\text{C}$  under vacuum for 5 days. The xerogel was coated with gold and its morphology was observed with JEOL JSM-840A scanning electron microscope (SEM) at the magnifications of 15 K and 20 K.

### 3. Results and discussion

In this study, we used UHMW S-PVA having nearly same  $P_n$  of 10,000 to clarify the effect of tacticity. Figure 1 shows  $T_{gm}$  of UHMW S-PVA/DMSO/water gel.  $T_{gm}$ s of UHMW S-PVA gels having S-diad contents of 61.5 and 58.2% did not reveal a great difference. However, the significant decrease of  $T_{gm}$  was found in the gel of UHMW S-PVA with S-diad content of 55.7%. From this result, it is obvious that gel melting depends on the syndiotacticity of UHMW S-PVA and the thermal resistance of PVA gel is enhanced when a highly syndiotactic PVA is used. Moreover, it is carefully suggested 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.

Physical gels have complex network junctions connecting polymer chains by segmental unit. The Eldridge-Ferry method<sup>25</sup> gives the total enthalpy of junction fusion,  $\Delta H_o$ , on gel melting from the slope of  $\ln c^*$  against  $1/T$ . It is known that  $\Delta H_o$  is proportional to the number of segments taking part in the junction,  $\zeta$ . Tanaka *et al.*<sup>26</sup> proposed the modified Eldridge-Ferry Eq. as following:

$$\ln c^* = \zeta \frac{\Delta h_o}{k_b T} - \frac{1}{s-1} \ln M + \text{constant} \quad (1)$$

where  $c^*$  is the gel melting concentration,  $T$  is the absolute temperature, and  $k_b$  is the Boltzmann constant,  $\Delta h_o$  is the enthalpy of bonding,  $s$  is the number of chains combined to a single junction, and  $M$  is the molecular weight, respectively. Figure 2 shows the Eldridge-Ferry plot of UHMW S-PVA/DMSO/water solution and the calculated values of  $\Delta H_o$  and  $\zeta$  from Eq. (1) are listed in Table 1. In case of hydrogels of A-PVA having  $P_n$  of 1,700-17,900, the  $\zeta$  value of 16.3 was obtained, which was independent of molecular weight<sup>26</sup>. However, the syndiotacticity of PVA had a strong effect on  $\zeta$  as shown in Table 1. In addition, UHMW S-PVA gel has a higher  $\zeta$  than UHMW A-PVA. The number of the syndiotactic units in a junction in PVA gel can increase strikingly when both the syndiotacticity and molecular weight of PVA are sufficiently high.

Figure 3 shows the change of  $G'$  of UHMW S-PVA gel with temperature. The higher value of  $G'$  was obtained in UHMW S-PVA gel with higher syndiotacticity at the same temperature. This may rise from the fact that the network in UHMW S-PVA gel with higher S-diad content is much tighter and closer as is postulated from the higher value of  $\zeta$ . Figure 3 also shows hysteresis curve of  $G'$  for 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<sup>27</sup>. It is quite noteworthy that  $G'$  increased under recooling and the recovery of  $G'$  about 70% was achieved when the temperature was lowered to  $25\text{ }^{\circ}\text{C}$  in both cases of 61.5% and 58.2% UHMW S-PVA gels. From the result in Figure 3, 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 reproducible under cooling after heating. In contrast, almost no recovery was found in 55.7% UHMW S-PVA gel, implying that hydrogen-bonding ability required to reform a stable gel network is relatively weak. Recovery of elasticity of 55.7% UHMW S-PVA gel may be achieved at the lower temperature.

Figure 4 shows the change of the light transmittance of UHMW S-PVA gel with aging time. The influence of syndiotacticity on the turbidity is evident. The significant decrease of transmittance was reported due to the phase separation followed by the crystallization<sup>15,30</sup>. The turbidity of PVA gel depends on the rate of gelation and phase separation<sup>30</sup>. If gelation occurs before phase separation, a homogeneous

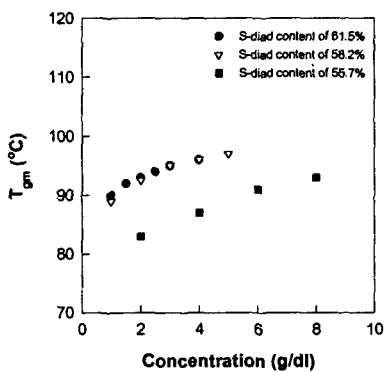
gel structure is developed and phase separation is greatly inhibited. If phase separation occurs faster than gelation, a gel becomes opaque. The significant decrease of transmittance is the evidence of the phase separation accompanied by the gelation of 61.5 and 58.2% UHMW S-PVA solution. It is evidently suggested that the syndiotactic configuration of UHMW S-PVA molecule promotes the phase separation, however, S-diad content of 55.7% is not high enough to cause the phase separation in the gelation process. This result is well coincident with those found in the in-situ fibrillation of PVA during saponification<sup>17, 18, 24, 31</sup>. The gradual decrease of the light transmittance is due to the crystallization at the gel phase with progress of aging time. It is considered from the series of experiments that a marked change was found in the characteristics and properties of UHMW S-PVA gel having S-diad content over 58.2%.

#### 4. References

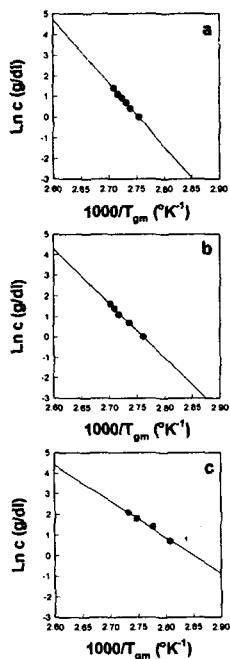
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**Table 1.** Characteristics of UHMW S-PVA gels

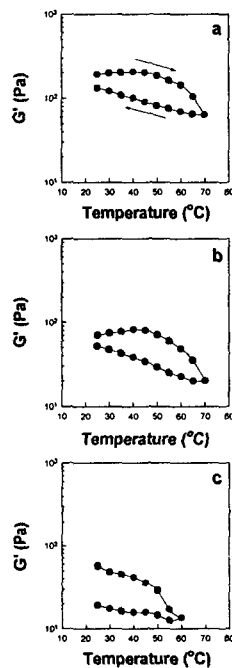
No	$P_n$	S-diad (%)	DS (%)	$\Delta H_o$ (kJ/mol)	$\zeta$
1	9,900	61.5	99.9	257.0	36.6
2	10,400	58.2	99.9	220.6	31.3
3	10,100	55.7	99.9	146.4	20.5



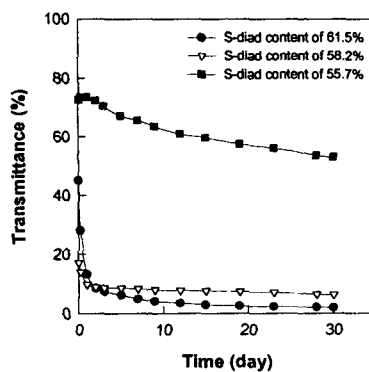
**Figure 1.** Effects of syndiotacticity and solution concentration on melting temperature of UHMW S-PVA/DMSO/water gel.



**Figure 2.** Eldridge-Ferry plot of UHMW S-PVA/DMSO/water gel: S-diad content: a, 61.5%; b, 58.2%; c, 55.7%.



**Figure 3.** Change of  $G'$  of 4.0 g/dl UHMW S-PVA/DMSO/water gel at the frequency of 1.0 rad/s with temperature: a, 61.5%; b, 58.2%; c, 55.7%.



**Figure 4.** Change of light transmittance of UHMW S-PVA gel (4.0g/dl) at 600nm with time at 0°C.