

Effect of Thermal Hysteresis on Melting of Syndiotacticity-Rich Poly(vinyl Alcohol) Hydrogel

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Synopsis

The melting temperatures (T_M) of hydrogels prepared by chilling aqueous solutions of syndiotacticity-rich poly(vinyl alcohol) (*s*-PVA) at 0°C were measured rising temperature of gels from the initiative temperature (T_I) of 0–70°C (every 10°C). The apparent enthalpies of fusion of a junction ΔH 's were estimated from the relation between the logarithm of polymer concentration ($\log C$) and $1/T_M$. ΔH depended on T_I , showing that the melting point of gels depended on a thermal hysteresis. The highest polymer concentration C_H in those of the gels which have no melting point above an initiative temperature was determined and ΔH was estimated from the relation between $\log C_H$ and the reciprocal melting point of the gels with C_H , $1/T_{IM}$. The ΔH was 15.1 kJ/mol in the range of higher polymer concentrations and 43.9 kJ/mol in the range of lower concentrations.

INTRODUCTION

In the previous papers,^{1–5} the authors have reported that an aqueous solution of syndiotacticity-rich poly(vinyl alcohol) (*s*-PVA) formed a hard elastic hydrogel easier than that a commercial poly(vinyl alcohol) (α -PVA) and that the melting point of the hydrogel of *s*-PVA was remarkably higher than that of α -PVA due to the junctions made of the longer syndiotactic sequences in *s*-PVA. The properties of gels are influenced by the molecular weight between junctions in networks, the number of junctions, and the size of junctions. Both the molecular weight between junctions and the number of junctions are correlated, i.e., the former decreases and the latter increases with the increase in Young's modulus.⁶ The size of junction in networks of PVA gel has been investigated by X-ray diffraction technique⁷ and Eldridge and Ferry's method.⁸ As the X-ray diffraction pattern of PVA gel was considered to give diffuse halos, the average size of gel junctions was obtained from the Guinier's plots using small angle X-ray diffraction.⁷ According to Eldridge and Ferry,⁸ the apparent enthalpy of fusion of junction of gel ΔH is estimated from the relation between the logarithm of polymer concentration $\log C$ and the reciprocal melting temperature $1/T_M$. In α -PVA, ΔH was 37 kJ/mol, which corresponds to one or two hydrogen bonds.⁹ The authors reported the ΔH values of PVA samples derived from vinyl acetate,^{1,10} vinyl trimethylsilylether,¹⁰ vinyl formate,^{1,5} and vinyl trifluoroacetate,^{1,2,5} to be 30–43, 34–41, 42–159, and 46–217 kJ/mol, respectively. In general, the measurement

of melting point of gel has been carried out rising temperature from the chilling temperature. The authors have found that *s*-PVA hydrogels with higher polymer concentrations showed syneresis with the rise in temperature,²⁻⁴ and that the shear modulus of *s*-PVA hydrogel chilled at lower temperatures showed the unique change with the rise in temperature. The values of ΔH for *s*-PVA hydrogel^{2,5,11} and *s*-PVA gels made from the solution with the mixtures of water/dimethyl sulfoxide (DMSO) or water/ethylene glycol (EG) systems¹¹ were found to depend on the chilling temperature (gelling temperature). The *s*-PVA hydrogels with lower contents of DMSO or EG had the lowest at a low gelling temperature and the largest ΔH at a high gelling temperature. Namely, the melting point of the *s*-PVA hydrogels chilled at lower temperatures was considered to depend on a thermal hysteresis.

In this paper, the melting points of *s*-PVA hydrogels chilled at 0°C were measured with rising temperature from initiative temperatures of 0–70°C (every 10°C), and the dependence of the initiative temperatures on ΔH was examined.

EXPERIMENTAL

Sample

An *s*-PVA derived from vinyl trifluoroacetate (VTFA) was used. The bulk polymerization of VTFA was carried out at 60°C by using benzoyl peroxide as an initiator. Poly(vinyl trifluoroacetate) was converted to PVA by dissolving it in 2,2'-diaminodiethylamine. The degree of polymerization was 1910 and the content of syndiotactic diad was 56.4%.

Melting Point of Gel

The apparent melting points of gels were determined according to Eldridge and Ferry's method.⁸ Solutions were obtained by dissolving a known amount of *s*-PVA at about 130°C in test tubes with 2.5 cm³ water. The polymer concentration was represented as g/dL, which was estimated considering the additivity of the volumes of water and PVA (the density in amorphous state: 1.269 g/cm³). The solutions were held for 24 h at 0°C. The test tubes were placed upside down in a well-stirred poly(ethylene glycol) bath that was warmed from the fixed temperature (0–70°C, every 10°C) at a rate of about 1°C per 5 min. The temperature at which the gel fell to the bottom of the test tube was taken as the melting point.

RESULTS AND DISCUSSION

Eldridge and Ferry have presented the following relation for the concentration C against the melting point of gel T_M :⁸

$$\log C = A - (\Delta H/2.303RT_M) \quad (1)$$

where A is constant, ΔH the apparent enthalpy of fusion of a junction in gel, and R the gas constant. The relations between the logarithm of C and the

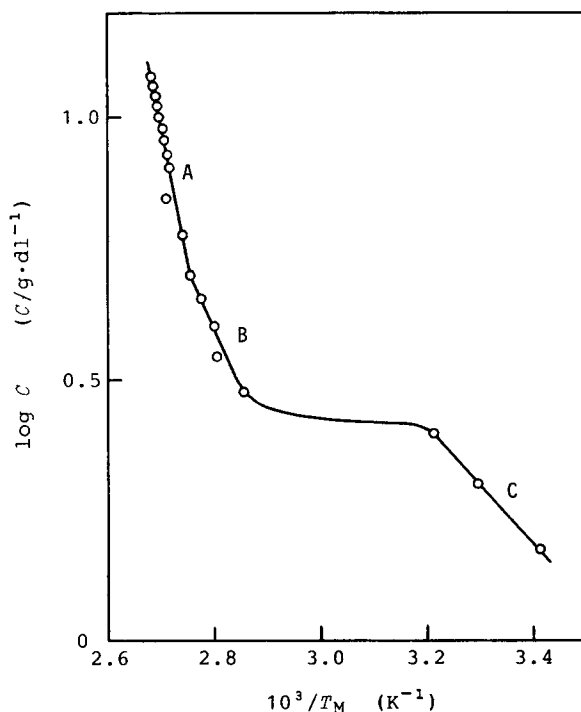


Fig. 1. Relation between the logarithm of polymer concentration $\log C$ and the reciprocal melting point $1/T_M$ at the initiative temperature of heating $T_I = 0^\circ\text{C}$ for *s*-PVA hydrogels chilled at 0°C .

reciprocal T_M are shown in Figures 1–4 in accordance with eq. (1). When the initiative temperature of heating T_I is 0°C , the plot of $\log C$ against $1/T_M$ separates into two regions as well as those in the previous papers.^{1,2,5} In the region of higher polymer concentrations, though the plot can be approximated by a straight line,^{1,2,5,11} if examined in detail it can be separated into two straight lines (regions A and B) as shown in Figure 1. This is recognized even in the case of $T_I = 10, 20,$ and 30°C (Fig. 2). The polymer concentration at the intersection of two straight lines is about 5 g/dL. Figures 3 and 4 show the relations between $\log C$ and $1/T_M$ for $T_I = 40$ and 60°C . At the initiative temperatures above 40°C , the plots of $\log C$ against $1/T_M$ are shown by a straight line in the range of higher polymer concentrations. In the region of lower polymer concentrations (region C), T_M depends on the polymer concentration C up to $T_I = 20^\circ\text{C}$ (see Fig. 1), but in the initiative temperatures over 30°C the gels fall down in the test tubes at the temperature near T_I .

So far, in order to understand the properties of *s*-PVA gel, we estimated ΔH in accordance with eq. (1).^{1,2,5,11} If ΔH does not depend on T_I , the value for the gel in which the sample, the molecular weight, and the solvent were specified is considered to represent a certain inherent value independent of T_I . Figure 5 shows the relations between ΔH and T_I . The measurement of melting point for *s*-PVA hydrogel was carried out twice and ΔH values shown in Figure 5 are mean values. In the region A (over $C = 5$ g/dL), ΔH was 92–100 kJ/mol at $T_I = 0$ – 30°C and decreased with the increase in the initiative

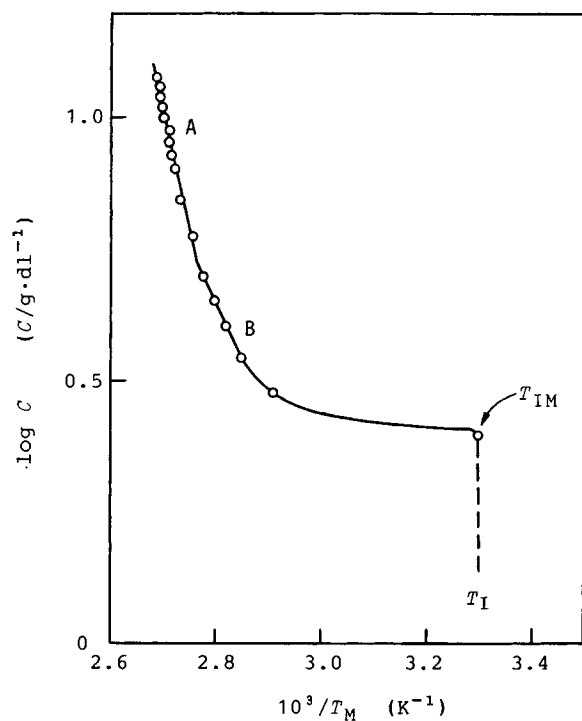


Fig. 2. Relation between $\log C$ and $1/T_M$ at $T_I = 30^\circ\text{C}$ for s-PVA hydrogels chilled at 0°C .

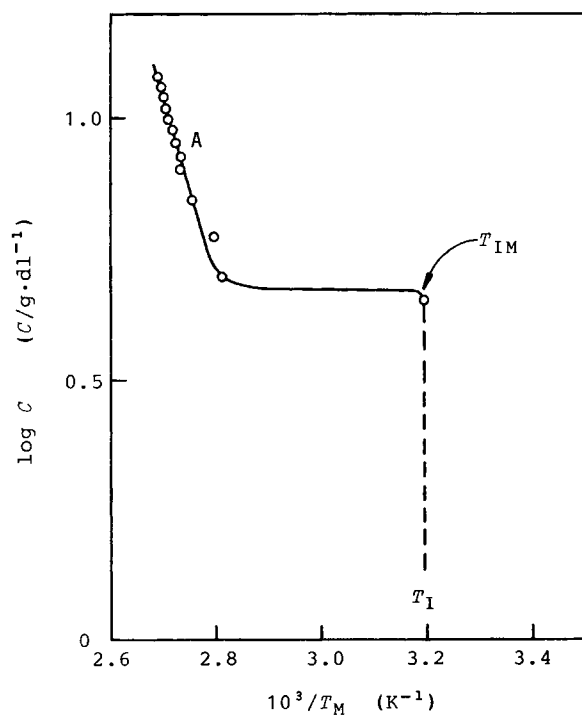


Fig. 3. Relation between $\log C$ and $1/T_M$ at $T_I = 40^\circ\text{C}$ for s-PVA hydrogels chilled at 0°C .

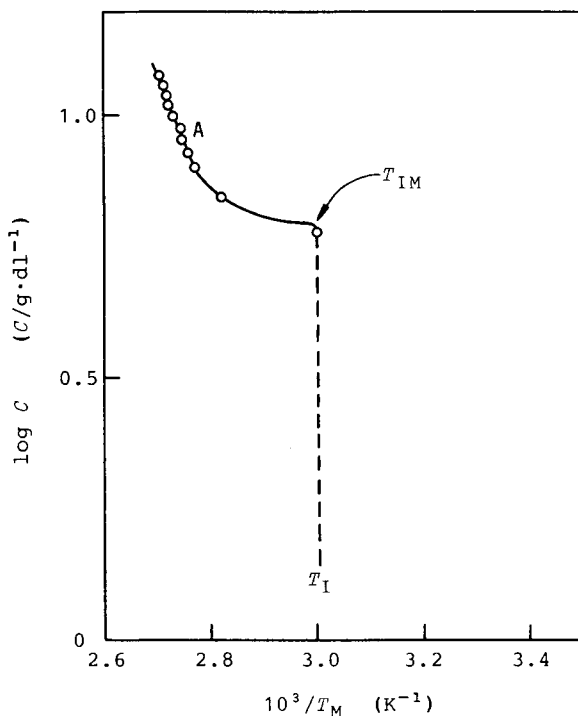


Fig. 4. Relation between $\log C$ and $1/T_M$ at $T_I = 60^\circ\text{C}$ for *s*-PVA hydrogels chilled at 0°C .

temperature at T_I over 30°C . In the region B, ΔH was minimum at $T_I = 20^\circ\text{C}$. Namely, ΔH depended on T_I . Those results suggest that ΔH obtained in Figure 5 does not represent the inherent value for an *s*-PVA hydrogel. Therefore, *s*-PVA hydrogels chilled at lower temperatures show a thermal hysteresis. Shibatani¹² measured the rigidity and the equilibrium swelling volume of gels as a function of gelling period and temperature, using a lightly crosslinked PVA sample, which bears repeated gelling and melting on a dynamometer, and recognized that with increasing temperature the tensile force of the gels increased at first and then fell rapidly. The result suggests that the lightly crosslinked PVA hydrogels show a thermal hysteresis.

As described above, at the initiative temperatures over 30°C gels with the concentration below a certain one fall down in the test tube at the temperature near T_I . T_{IM} 's shown in Figures 2-4 are considered as the melting point of the gel. Figure 6 shows the relation between the logarithm of the polymer concentration of the gels with the melting point T_{IM} , $\log C_H$, and $1/T_{IM}$. ΔH was also estimated in accordance with eq. (1). ΔH was estimated to be 15.1 kJ/mol in the range of higher polymer concentrations whereas it was estimated to be 43.9 kJ/mol in the range of lower concentrations. From the melting points of gels obtained, increasing the temperatures from 0 or 30°C , ΔH of gels of higher polymer concentrations (region A) was recognized to be higher than that of lower polymer concentrations (region B) (see Figs. 1 and 2). If ΔH obtained from the result shown in Figure 6 reflects the structure of raw gels, the size of junctions in the range of higher polymer concentrations should be smaller than that in the range of lower polymer concentrations: i.e.,

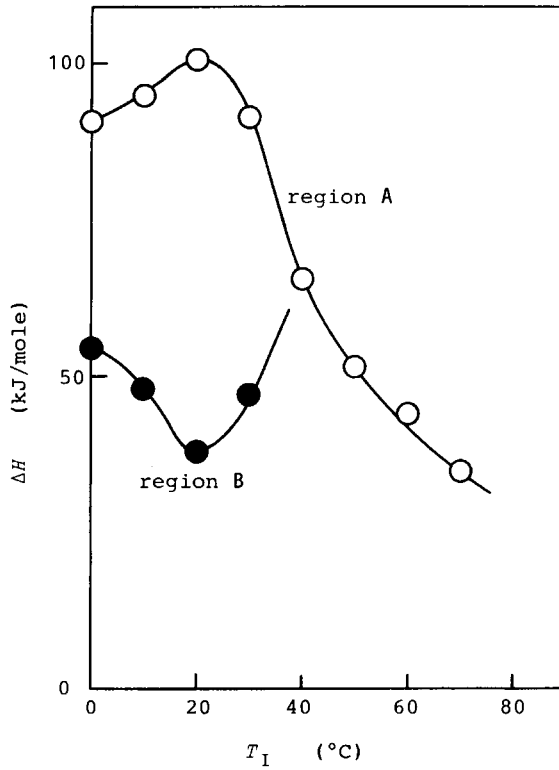


Fig. 5. Relation between the apparent enthalpy of fusion of a junction ΔH and T_I for s-PVA hydrogels chilled at 0°C.

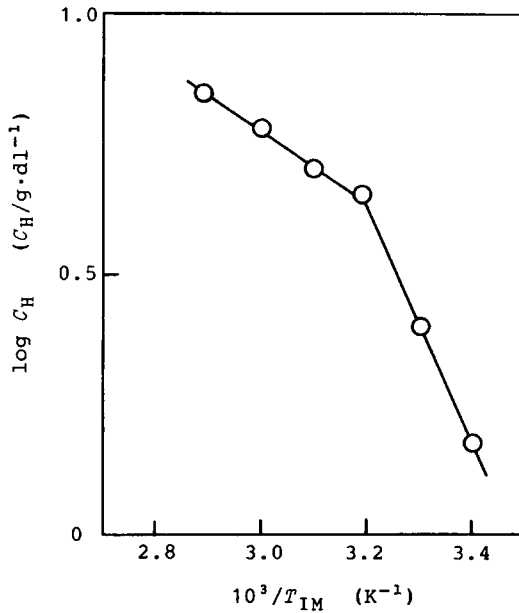


Fig. 6. Relation between $\log C_H$ and $1/T_{IM}$ for s-PVA hydrogels chilled at 0°C.

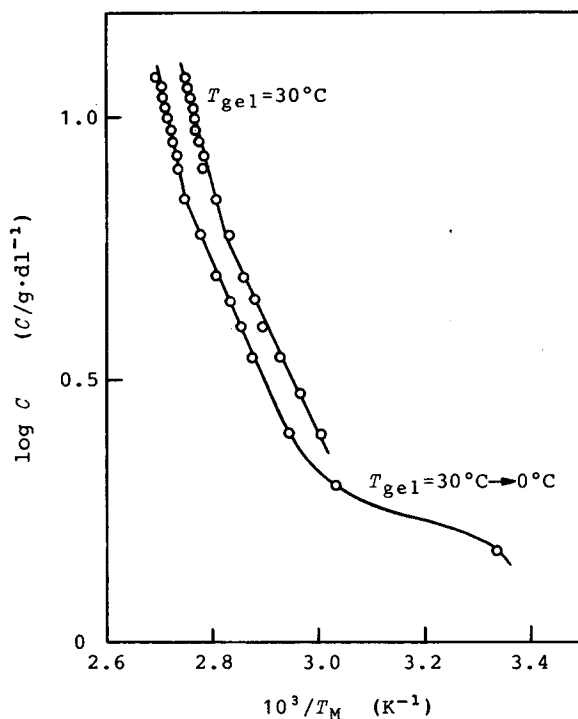


Fig. 7. Relation between $\log C$ and $1/T_M$ at $T_I = 30^\circ\text{C}$ for hydrogels chilled at 30°C , and at $T_I = 0^\circ\text{C}$ for hydrogels chilled at first at 30°C and then at 0°C .

the size of junction of network in the gel with higher polymer concentration is small and the number of junction is numerous. ΔH of the gels chilled at lower temperatures is considered to become high as shown in Figure 5 due to the growth of junction. The junction size of network in the gel with low polymer concentration (Fig. 6) coincides roughly with that in the gel heated from higher T_I (Fig. 5); therefore, the propagation of junctions in the gel with low polymer concentration is lower than that in gel with high polymer concentration. As the bond energy of a hydrogen bond is about 21 kJ/mol, $\Delta H = 15.1$ kJ/mol obtained in the range of higher polymer concentrations in Figure 6 is too small for a junction of network in gels. These results must be confirmed by prospective, detailed experiments. Shibatani¹² showed that the number of network chains in the lightly crosslinked PVA hydrogels decreased, and the sequence lengths of syndiotactic units in a junction increased with the increase in the gelling temperature.

The authors examined the relation between ΔH and the gelling temperature, and recognized that ΔH gave the smallest at the gelling temperature $T_{\text{gel}} = 30^\circ\text{C}$. Figure 7 shows the relations between $\log C$ and $1/T_M$ for gels chilled at 30°C and for gels chilled at first at 30°C and then at 0°C . ΔH 's obtained using Figure 7 are shown in Table I with ΔH of gel chilled at 0°C . ΔH for gels chilled at 30°C is lower than that for gels chilled at 0°C the same as the results described in the previous paper.^{2,11} For gels chilled at 30°C followed by at 0°C , ΔH was higher than that chilled at 30°C , but lower than that chilled at 0°C . From this result it is also expected that the gel shows a

TABLE I
Enthalpy of Fusion of a Junction ΔH for Hydrogels Obtained
under Various Chilling Conditions

Chilling temp (°C)	ΔH (kJ mol ⁻¹)	
	Region A	Region B
0	92.9	49.4
30	81.3	37.6
30 → 0	90.0	43.2

thermal hysteresis. However, the junctions of the network that formed in the gel obtained by chilling at 30°C interfere partially with the additional gelation at 0°C.

CONCLUSION

In order to estimate the size of junction of network in gels, so far Eldridge and Ferry's method⁸ and Takahashi et al.'s method¹³ have been used by many researchers for PVA samples of different stereoregularities–water systems,^{1-7,9-11,14} dimethyl sulfoxide/water or ethylene glycol/water mixed solvent–*s*-PVA system,¹¹ various solvent–poly(vinyl chloride) systems,¹³ various solvent–ethylene–vinylacetate copolymer systems,¹⁵ various solvents–branched polyethylene systems,¹⁶⁻¹⁸ and various solvents–atactic polystyrene systems.¹⁹ All these methods were carried out by the measurement of melting point in the rise of temperature from the chilled temperature. In the case of *s*-PVA, ΔH obtained from eq. (1) depended on the initiative temperature of heating. The fact suggests that the junction of network in gel dissolves and grows in the rise of temperature, that is, it shows thermal hysteresis. Therefore, the melting point of gel must be measured after the confirmation that it does not depend on a thermal hysteresis or by the method that it does not depend on a thermal hysteresis. Such a method will be accomplished as follows; first one holds gels with various polymer concentrations at fixed temperatures, and then measures a boundary polymer concentration at which the gels melt or not. The gel with the boundary polymer concentration is considered hardly to show a thermal hysteresis at the fixed temperature.

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