

Melting, Regelling, and Remelting of Poly(vinyl alcohol) Hydrogels

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SYNOPSIS

The melting behaviors of hydrogels of syndiotacticity-rich poly(vinyl alcohol) (*s*-PVA), derived from vinyl trifluoroacetate, during heating at various rates of rising temperature were examined. For the hydrogels with the polymer concentrations above 5 g/dL chilled at the temperatures of 0 ~ 40°C, the melting temperature increased with a decrease in the rate of rising temperature. During rising temperature at lower rates, the phase separation with spinodal decomposition progressed even in gels and the microcrystals, which play an important role as the junction points, propagated to thermally more stable size. The small, broad exothermic peaks during rising temperature of *s*-PVA hydrogels in DSC thermograms was found at the temperature ranges of 10 ~ 30 and 45 ~ 60°C. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

The solutions of poly(vinyl alcohol) (PVA) have been well known to gel by standing for a long time at lower temperatures, and various studies have been performed to understand the mechanical and thermal properties of the gels.¹⁻⁴ Authors performed the studies for the hydrogels of syndiotacticity-rich PVA (*s*-PVA) derived from vinyl trifluoroacetate,⁵⁻¹⁶ and the curves of the relation between the melting temperature T_M of gels and the polymer concentration C have been found remarkably to separate in higher and lower polymer concentration regions.^{5,7,11,13,14} In the region of higher polymer concentrations, the fusion enthalpy ΔH obtained from the $\ln C - 1/T_M$ relation presented by Eldridge-Ferry¹⁷ was effected by the preparation conditions of gels and the stereoregularity of polymer. In the region of lower polymer concentrations, the gelation was considered to occur by connecting water molecules between polymer chains.⁵ However, it has been clarified that the melting temperature of *s*-PVA hydrogels was influ-

enced by the heating process.^{11,13,14} The most stable *s*-PVA hydrogels were found to be formed by chilling at 40–50°C with the result that the bending and shearing modulus of the gels changed peculiarly during heating from 0°C,^{10,11} *s*-PVA hydrogels with dimethyl sulfoxide regelled seldom after melting during rising temperature,¹⁴ the melting temperature for the *s*-PVA hydrogels chilled at lower temperatures lowered with an increase in the initiative temperature of heating,¹³ and the *s*-PVA casting-films elongated peculiarly during rising temperature in water.^{18,19} The thermodynamical interpretation of those results has already been shown in the previous paper.¹¹ Moreover, the study of solution viscosity has resulted in the conclusion that the interaction between *s*-PVA and water molecules was weak at about 50°C.²⁰

In the present study, the range of polymer concentration for the regelation after melting of *s*-PVA hydrogels, the effect of the rate of rising temperature on the regelation, and the relations between the regelation or remelting temperatures and the rate of rising temperature were examined. Moreover, the melting and regelation were also examined by using a high sensitive differential scanning calorimetry (DSC) apparatus.

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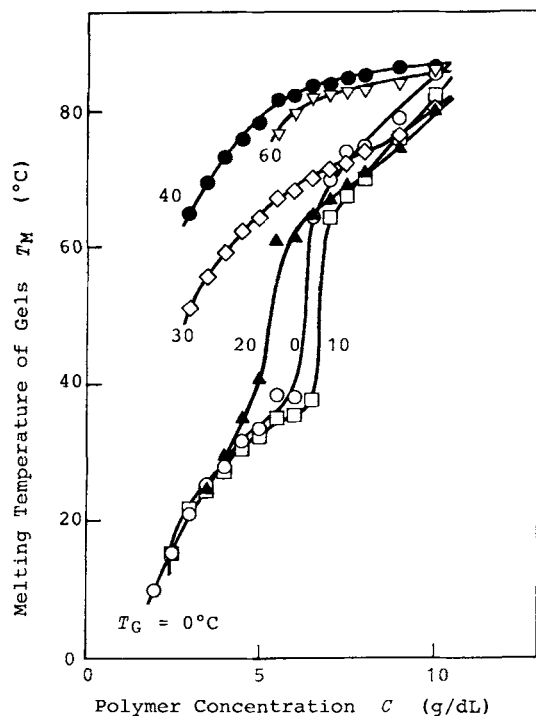


Figure 1 Relation between the melting temperature and the polymer concentration for *s*-PVA hydrogels obtained at various chilling temperatures (rate of rising temperature: 0.33°C/min).

EXPERIMENTAL

Sample

An *s*-PVA derived from vinyl trifluoroacetate (VTFA) was used as a sample. The VTFA monomer was polymerized in bulk at 60°C employing benzoyl peroxide as an initiator. Poly(vinyl trifluoroacetate) was converted to *s*-PVA by dissolving it in 2,2'-diamino diethylamine. The degree of polymerization and the content of syndiotactic dyad were 730 and 57%, respectively.

Melting Points of Gels

Each 2.5 mL of water and each fixed amount of *s*-PVA were added to glass tubes (10 mm i.d.) and sealed at 7 cm from the bottom. The polymer was dissolved in water in a well-stirred polyethylene glycol (PEG) bath heated at 130°C. The solutions were chilled at 0 ~ 60°C for 24 h. The melting points of gels were determined at the rates of rising temperature of 0.2 ~ 1.5°C/min from the chilling temperatures (gelling temperatures: T_G) in a water bath (0

~ 25°C) or a PEG bath (>25°C) after the glass tubes with gels were put upside down. The temperature at which a gel fell to the bottom of the tube after air entered inside it was regarded as the melting temperature T_M .

Differential Scanning Calorimetry

DSC was carried out with a highly sensitive DSC 8240 B from Rigaku Co. Ltd. The *s*-PVA hydrogels used were prepared by chilling at 0°C for 24 h the aqueous solutions with the polymer concentrations of 5 ~ 8 g/dL. About 25 mg each of hydrogels were sealed into aluminum pans. The temperature was raised from -5 to 100°C at a rate of 1°C/min, and the measurable range was 0.1 mcal/s.

RESULTS AND DISCUSSION

Effect of Chilling Temperature on Melting Temperature of Gels

Figure 1 shows the relation between the melting temperature and the polymer concentration for the

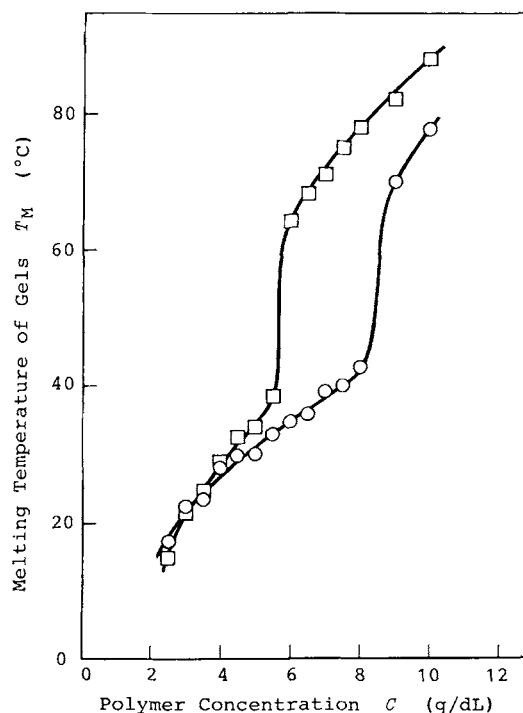


Figure 2 Relation between the melting temperature and the polymer concentration for *s*-PVA hydrogels obtained at a chilling temperature of 0°C. Rate of rising temperature: (○) 1.5°C/min; (□) 0.25°C/min.

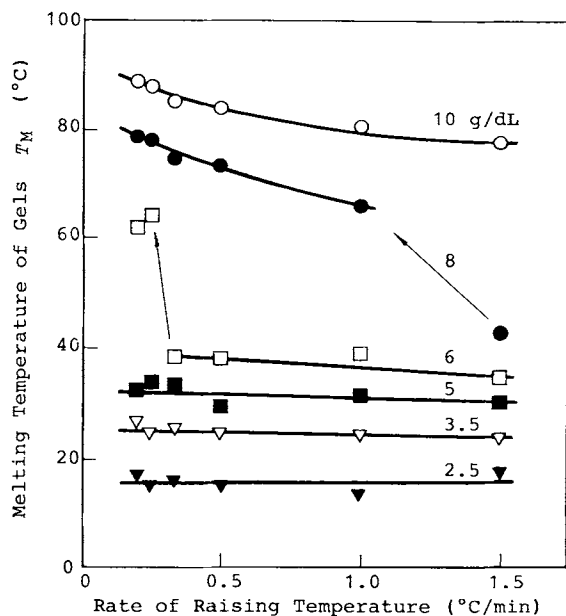


Figure 3 Relations between the melting temperature and the rate of rising temperature for *s*-PVA hydrogels obtained at a chilling temperature of 0°C.

hydrogels prepared by chilling at $T_G = 0 \sim 60^\circ\text{C}$. For the hydrogels prepared by chilling at the temperatures of $T_G = 0, 10$ and 20°C , each curve separated clearly into two regions similar to the results found previously.^{5,7,11,13,14} In the present study, especially, the melting temperature was nearly equal for those gels with the lower, same polymer concentrations. The mobility of polymer chains of *s*-PVA is considered to be very low below 20°C in the aqueous solution.²⁰ For the hydrogels prepared by chilling at the temperatures of 30 and 40°C , each curve was smooth, and the melting temperatures of gels with the same polymer concentrations increased with an increase in the chilling temperature in the range of the low polymer concentration. The thermally most stable gels were obtained by chilling at $40 \sim 50^\circ\text{C}$. This result coincided with the result of solution viscosity that the interaction between *s*-PVA and water molecules was weak at about 50°C .²⁰ Namely, the phase separation with spinodal decomposition²¹ is considered to occur slowly and/or easily at about 50°C for aqueous *s*-PVA solutions, and then the solutions gel. Therefore, the thermally most stable junction points are formed in the region of higher polymer concentrations by chilling at about 50°C for the *s*-PVA aqueous solutions. When the chilling temperature is over 60°C , the critical lowest polymer concentration of gelation and the melting

temperature lower with an increase of chilling temperature. This is attributed to the activated thermal motion of polymer chains.

The quick chilling to lower temperatures leads to the gelation of solution in very short time so that the phase separation with spinodal decomposition is impossible.²² Therefore, the formation of junction points with short length has preference and prevents the formation of the thermally stable, longest junction points. The aqueous *s*-PVA solutions gel in a very short time compared with the aqueous solutions of atactic PVA derived from vinyl acetate.

Effect of Heating Rate of Melting Temperature of Gels

Figure 2 shows the relation between the melting temperature and the polymer concentration for the hydrogels prepared by chilling at 0°C . In Figure 2, the results for only two typical rates of rising temperature are shown. In the range of the polymer concentrations below 5 g/dL , T_M was independent on the rate of rising temperature and nearly equal at same polymer concentrations. However, in the range of polymer concentrations above 5 g/dL , T_M was dependent on the rate of rising temperature. These results are detailed in Figures 3 and 4. Figures

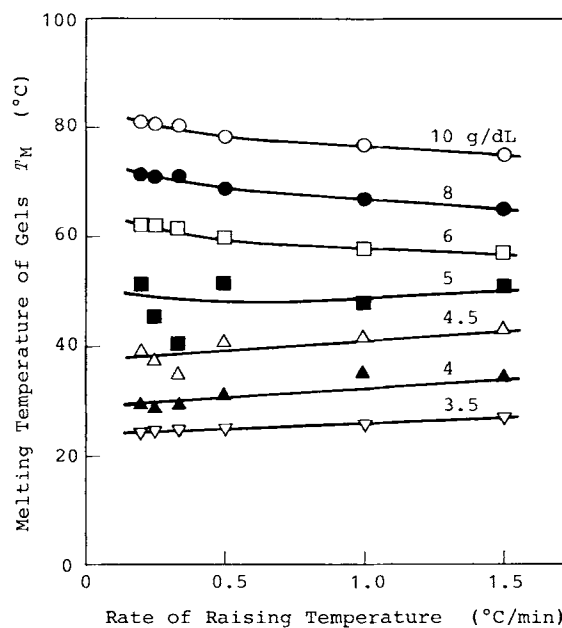


Figure 4 Relations between the melting temperature and the rate of rising temperature for *s*-PVA hydrogels obtained at a chilling temperature of 20°C .

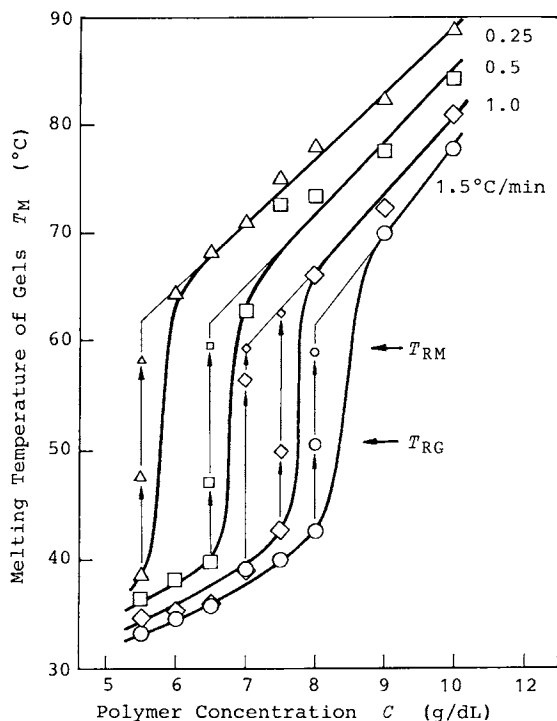


Figure 5 Relations between the melting, regelling, or remelting temperatures (T_M , T_{RG} , or T_{RM}) for *s*-PVA hydrogels obtained at a chilling temperature of 0°C.

3 and 4 show the relation between the melting temperature and the rate of rising temperature for the hydrogels prepared by chilling at 0 and 20°C, respectively. Although the melting temperature was independent of the rate of rising temperature for the hydrogels prepared by chilling at 0°C with the polymer concentrations below 5.5 g/dL, it increased slightly with an increase in the rate of rising temperature for the hydrogels prepared by chilling at 20°C. The junction points in the latter hydrogels were thermally stable, and the rising temperature at higher rate brought about superheating. For the hydrogels with the polymer concentrations above 6 g/dL, however, the melting temperature increased with a decrease in the rate of rising temperature and this result was contrary to the general conception. It is imagined that structures formed newly in gels or the junction points propagated at lower rates.¹¹ The similar results were found at the polymer concentrations over 5 g/dL for the hydrogels prepared by chilling at 30 and 40°C. The phase separation with spinodal decomposition was considered to propagate even in gels during heating from 0 ~ 40°C to 50°C.

In Figure 3, inasmuch as the melting temperature was not obtained in the rates of rising temperature between 0.20 ~ 0.33 and 1.0 ~ 1.5°C/min for polymer concentration of 6 and 8 g/dL, those regions are drawn by spurious arrows.

Regelling and Remelting Through Heating

Figures 5 and 6 show the relation between the melting temperature and the polymer concentration for the hydrogels prepared by chilling at 0 and 10°C at various rates of rising temperature. The hydrogels with lower melting temperatures regelled during continuous rising temperature after melting in the narrow range of high polymer concentration. The regelling temperatures T_{RG} and the remelting temperatures T_{RM} are shown in Figures 5 and 6, respectively. The solutions after melting were still translucent and had supermolecular order (SMO)²³ as microcrystals or gel particles. During rising temperature, the spinodal phase separation progresses, the micro-crystals propagate again to junction points, and the solutions gel again at 45 ~ 52°C. The temperatures coincided with the chilling tem-

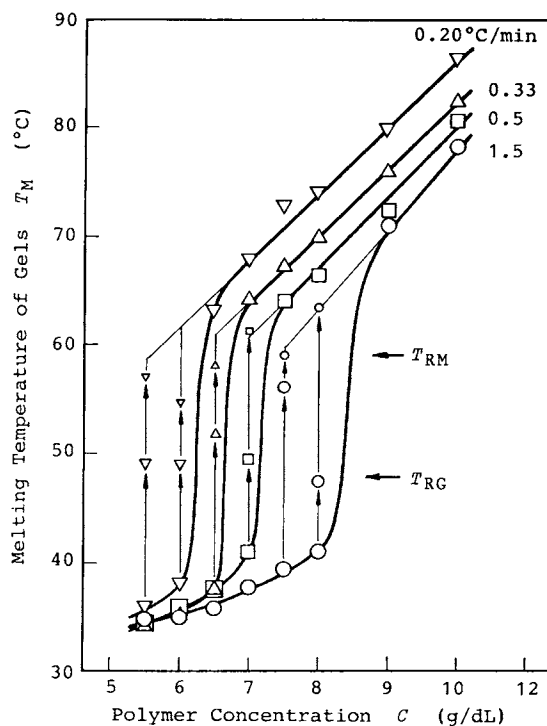


Figure 6 Relations between the melting, regelling, or remelting temperatures (T_M , T_{RG} , or T_{RM}) for *s*-PVA hydrogels obtained at a chilling temperature of 10°C.

peratures for the hydrogels that had the highest melting temperatures as shown in Figure 1. The gels remelt during continuous rising temperature and change to transparent solutions at higher temperatures over 100°C. The remelting temperatures did not exceed the extrapolated lines in the range of higher melting temperatures as shown in Figures 5 and 6. Namely, the *s*-PVA hydrogels form thermally stable junction points during rising temperature,¹¹ especially at lower rates. T_{RG} and T_{RM} had not the specific relations to the rate of rising temperature and are delicately influenced by thermal history.

Differential Scanning Calorimetry

Figure 7 shows the DSC thermograms for the hydrogels prepared by chilling at 0°C. The symbols ∇ , Δ , and \blacktriangledown in Figure 7 correspond to the melting, regelation, and remelting temperatures in Figure 5, respectively. A broad exothermic peak during rising temperature in the DSC thermograms is found at 10 ~ 30°C for the hydrogels with the polymer concentrations of 5.5 ~ 8 g/dL, and during continuous rising temperature a small, weak endothermic peak is found for the hydrogels with the polymer concentrations of 5.5 ~ 7.5 g/dL. Although the small endothermic peak did not coincide with symbol ∇ , the hydrogels melt at the neighborhood of the peak. During continuous rising temperature, the broad, small peak is found at 45 ~ 60°C in the thermograms for the hydrogels with the polymer concentrations of 7 and 7.5 g/dL, and the formation of SMO and the propagation of microcrystals are expected. The regelation was confirmed from the coincidence of the peak and symbol Δ . During continuous rising temperature, a broad, unclear endothermic peak was found in the thermograms for the solutions with the polymer concentrations of 5.5 and 6 g/dL, and a broad, distinct endothermic peak was found at 70 ~ 90°C for the hydrogels with the polymer concentrations of 7 ~ 8 g/dL. However, the melting temperatures of gels, symbols \blacktriangledown and ∇ , did not coincide with the broad, distinct endothermic peak. It is expected that the solutions have thermally stable SMO until considerable high temperatures of 80 ~ 90°C. In the case of 8 g/dL hydrogels that did not fall down in a glass tube at low temperature, no small endothermic peak was found in the thermograms. In the case of *s*-PVA hydrogels with polymer concentrations below 6.5 g/dL, no regelation was found during rising temperature. Therefore, the endothermic peak at 70 ~ 90°C was small and indistinct.

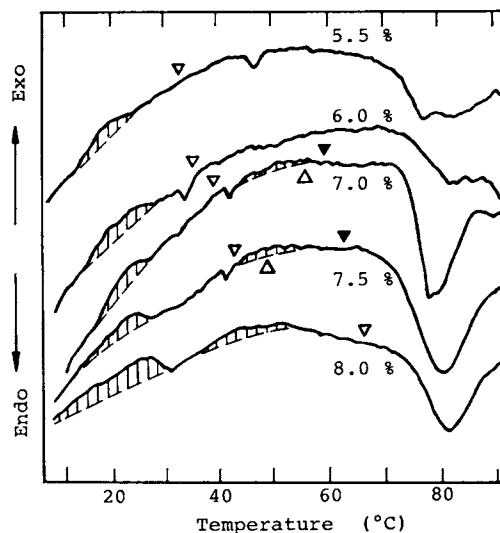


Figure 7 Thermograms for *s*-PVA hydrogels obtained at a chilling temperature of 0°C. Rate of rising temperature: 1°C/min; (∇) melting temperature; (Δ) regelation temperature; (\blacktriangledown) remelting temperature.

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