Effect of Addition of Saccharose on Gelation of Aqueous Poly(vinyl alcohol) Solutions

KAZUO YAMAURA,[1,*] MASAMI MITSUISHI,[1] MARI FUKUDA,[1] TETSUYA TANIGAMI,[1] YOSHIO HOEI,[2] and SHUIJI MATSUZAWA[1]

[1]Faculty of Textile Science and Technology, Shinshu University, 3-15-1 Tokida, Ueda-city, Nagano-prefecture 386, Japan; and [2]S & S Japan Co., Ltd., 6-1-18 Hamazoe-dohri, Nagata-ku, Kohbe-city, Hyogo-prefecture 653, Japan

SYNOPSIS

The properties of poly(vinyl alcohol) (PVA) hydrogels containing saccharose were examined. The effect of the addition of saccharose to atactic PVA (a-PVA) gels on their melting temperatures was larger than that for syndiotacticity-rich PVA (s-PVA) gels and the melting temperature was above 100°C for a-PVA gels with saccharose contents of 60 wt %. However, the fusion enthalpy (ΔH) of the a-PVA gels was at most 100 kJ/mol. The release of solvent (water/saccharose) from gels in air decreased with an increase in the saccharose content and the equilibrium was achieved after standing for 20 days for the a-PVA and s-PVA gels with saccharose contents above 40 and 20 wt %, respectively. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

The concentrated aqueous solutions of atactic poly(vinyl alcohol) (a-PVA) derived from vinyl acetate have been well known to gel after standing for a long time at 0°–25°C.[1-6] The melting temperature of the gels was low (below 50°C). Nambu[7] found that the melting temperature and the modulus of the gels prepared by freezing/thawing aqueous a-PVA solutions were higher than that of the gels chilled at temperatures above 0°C. Hyon and Ikada[8] and Yamaura et al.[9] found that the melting temperature and the modulus of the a-PVA hydrogels containing dimethyl sulfoxide were higher than that of the a-PVA hydrogels prepared at temperatures above 0°C. Water molecules in PVA hydrogels vaporize in air as the volume of gels decreases during the standing time until a solid polymer remains. The volume change in hydrogels and the syneresis of water from hydrogels during use as a covering medium for maintenance of low temperatures is unfavorable.

The present study examines the effects of the addition of saccharose on the melting temperature of PVA hydrogels and the volume change of PVA hydrogels with standing in air. Moreover, the prop-

erties of the PVA hydrogels with saccharose are examined.

EXPERIMENTAL

Samples

Two a-PVAs were used, which had the degree of polymerization (DP) of 1530 and 2400, and the syndiotactic dyad content [s-(dyad)] of ca. 45%. A syndiotacticity-rich PVA (s-PVA) derived from vinyl trifluoroacetate was used, in which DP = 1830 and s-(dyad) = 55%.

Distilled water was used as a solvent. Saccharose was special grade (Wako Pure Chemical Industrial, Ltd. Japan). The a- and s-PVAs were dissolved in an aqueous solution containing saccharose in a well-stirred poly(ethylene glycol) (PEG) bath. The dissolution temperature (T_D: ca. 110°–127°C) of s-PVA increased with an increase in the saccharose content (0–50 wt %) and was over 130°C in the case of saccharose content of 60 wt %. a-PVA is well-known to dissolve in water more easily than s-PVA. T_D of a-PVA (polymer concentration: C = 5–10 g/dL) was almost independent of the polymer concentration, ca. 60°–80°C (saccharose contents: 0–60 wt %), and increased with an increase in the saccharose contents. Namely, the addition of saccharose lowers the solubility of PVA in water.

Melting Points of Gels

The PVA solutions described above were warmed at 120°C in a well-stirred PEG bath and gelled by chilling at 0°–40°C for 24 h. The test tubes with gels were placed upside down in a well-stirred water bath. The bath was warmed from 0°C to 25°C at a rate of about 1°C/5 min. At temperatures above 25°C, the test tubes with gels were placed in a well-stirred PEG bath and warmed at the same rate. The temperature at which a gel fell to the bottom of the tube after air entered it was regarded as the melting temperature, T_m.

Dynamic Modulus

Dynamic compressive modulus was measured with a TMA 4000 apparatus from MAC Science Co., Ltd. Japan. After three cycles of the freezing/thawing process, the Young's modulus of the a-PVA gels obtained was measured from room temperature (ca. 25°C) to 50°C at a heating rate of 5°C/min. The load was 4 g and forced longitudinal vibration (sine wave) was 0.25 Hz. Moreover, the compressive moduli of the gels preserved in water and the freeze-dried gels were also measured.

Solvents Preserved in Gels

15 ml portions of a-PVA (C = 4, 5, 10 g/dL) or s-PVA (C = 2, 4 g/dL) solutions were poured into plastic photo-film cases (diameter: 2.9 cm). The cases with solutions were held in a freezer at −34°C for 18 h and thawed at room temperature for 6 h. This freezing/thawing process is one cycle. After three cycles, the gels obtained were put into a beaker covered by aluminum foil with many pinholes, stood in air at room temperature, and weighed after standing for 2 suitable number of days. The solution that transuded on the gel surfaces was wiped off by filter paper before weighing.

Differential Scanning Calorimetry

Differential scanning calorimetry (DSC) was carried out with a DSC 3200 apparatus from MAC Science Co., Ltd. Japan. One hundred mg each of saccharose/water solutions and PVA/saccharose/water solutions were sealed into silver pans. After cooling rapidly to −100°C and standing for 20 min at that temperature, the temperature of the sample pans was raised from −100°C to 50°C at a heating rate of 5°C/min. Seventy to 80 mg each of as-molded gels, equilibrium-syneresis gels, freeze-dried gels,

and dry gels were sealed into aluminum pans. The temperature was raised from −100°C to 300°C at a heating rate of 10°–20°C/min. Alpha alumina was used as a reference material.

RESULTS AND DISCUSSION

Melting Temperature of Gels

Figure 1 shows the relations between the melting temperature and the polymer concentration for the a-PVA gels chilled at 0°C. The melting temperature was below 30°C for gels with saccharose contents below 30 wt % and above 80°C for gels with saccharose contents above 50 wt %. The addition of saccharose into aqueous PVA solutions enhances the thermal stability of the gels. If a saccharose molecule is assumed to hydrate with five H_2O molecules,[10] the water molecules per vinyl alcohol unit is ca. 6 at the polymer concentration of 7.5 g/dL that corresponds to the transition point for the a-PVA solutions with saccharose contents of 40 wt % (Fig. 1). Recently, we have reported that six water molecules were estimated to bind with a base unit of PVA.[11]

The effect of the chilling temperature on the melting temperature of gels was examined. In the region of the saccharose contents of 10–30 wt %, the critical polymer concentration of gelation and
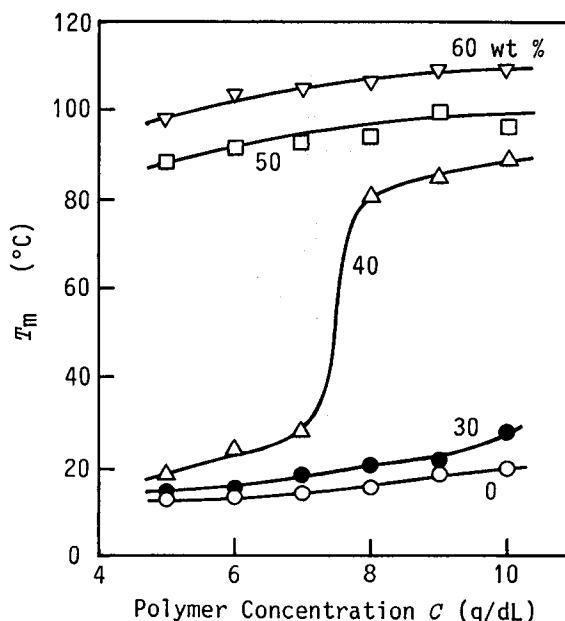

Figure 1   Relations between melting temperatures and polymer concentrations for a-PVA (DP = 1530) gels chilled at 0°C for 24 h. Numerals in figure are saccharose contents.
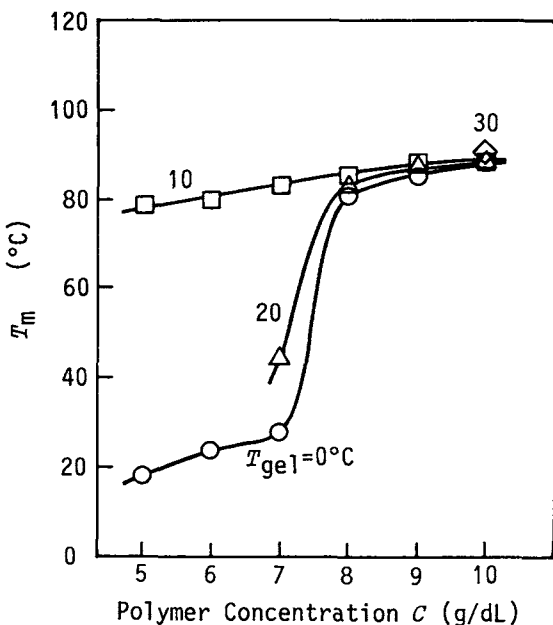
Figure 2 Relations between melting temperatures and polymer concentrations for a-PVA (DP = 1530) gels with saccharose contents of 40 wt % chilled for 24 h. Numerals in figure are chilling temperatures.

Figure 4 Relations between melting temperatures and polymer concentrations for s-PVA gels with saccharose contents of 10 wt % chilled for 24 h. Numerals in figure are chilling temperatures.

the melting temperature of gels increased with an increase in the chilling temperature. Similar results have been already obtained for s-PVA hydrogels.[12] Though the mobility of PVA chains enhances with

the rising temperature and the gelation ability lowers, the fewer but larger junctions are slowly formed. In the case of a-PVA gels with saccharose contents of 50–60 wt %, the effect of the chilling temperature (0°–40°C) on the melting temperature is very low and the melting temperature was nearly equal. Figure 2 shows the relations between the melting temperature and the polymer concentration for a-PVA
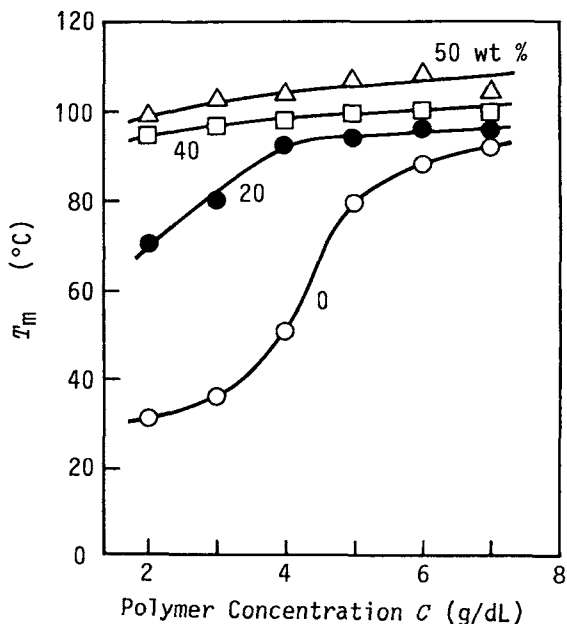

Figure 3 Relations between melting temperatures and polymer concentrations for s-PVA gels chilled at 0°C for 24 h. Numerals in figure are saccharose contents.
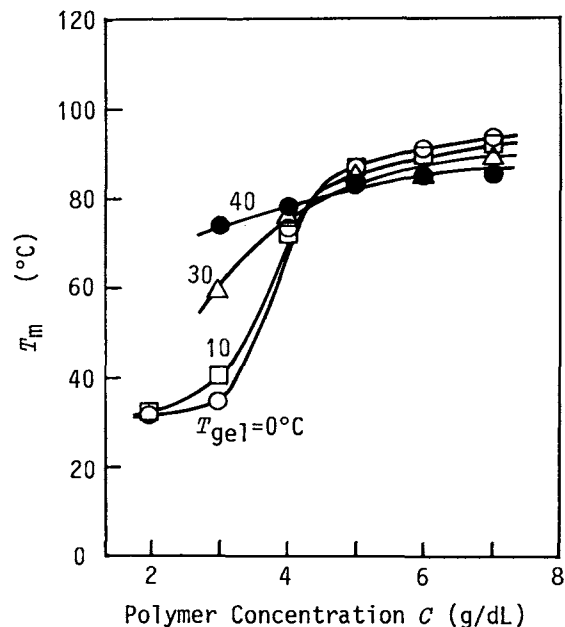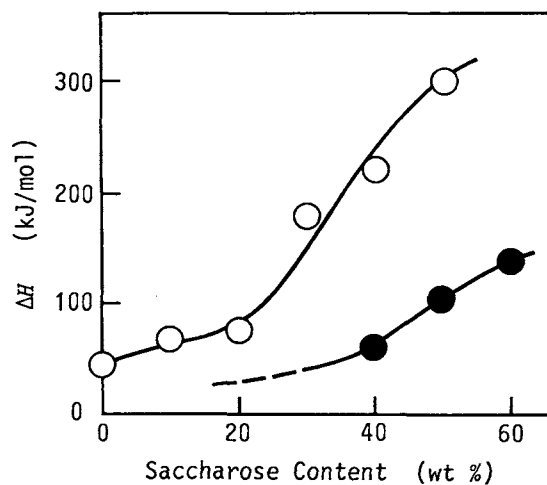

Figure 5 Relations between mean fusion enthalpy ΔH and saccharose contents for s-PVA and a-PVA (DP = 1530) gels chilled at 0°–40°C. ○ s-PVA, ● a-PVA.

Table I   Dynamic Compressive Modulus of a-PVA Hydrogels With or Without Saccharose from 25°C to 50°C and Transparency of Gels. (Initial Saccharose Content: 50 and 0 wt %; Initial Polymer Concentration: 5 g/dL.)

	Gels with Saccharose	Gels without Saccharose
(a) As-frozen/thawed gels	40 kPa	30 kPa
	Transparent	Transparent
(b) Freeze-dried gels of (a)	80 kPa	2–1 MPa
	Translucent	Chalky
(c) Gels of (b) preserved in water	45 kPa	180 kPa
	Translucent	Chalky + Transparent

gels with saccharose contents of 40 wt %. The effect of the chilling temperature on the gelation was very complicated.

Figure 3 shows the relations between the melting temperatures and the polymer concentrations for the s-PVA gels, chilled at 0°C, with saccharose contents of 0–50 wt %. The relations were similar to those shown in Figure 1, but the transition point was already recognized at the low polymer concentration. Namely, the interaction between s-PVA polymers is higher than between a–PVA polymers. Figure 4 shows the relations between the melting temperatures and the polymer concentrations for the s-PVA gels chilled at 0°–40°C. The melting temperature increased with an increase in the chilling temperature at polymer concentrations below 3 g/dL and with a decrease at polymer concentrations above 5 g/dL. The thermally stable gels are formed at higher chilling temperatures for the solutions with lower polymer concentrations or obtained during the propagation of junction through the heating process for gels with higher polymer concentrations.[12] For s-PVA gels with saccharose contents of 50 wt %, the effect of the chilling temperature on the melting temperature was not remarkable and the melting temperature was ca. 100°C.

Figure 5 shows the relations between the enthalpy of the thermal dissociation of the junctions of the spatial network, ΔH estimated by Eldridge-Ferry equation,[13] and the saccharose content for a- and s-PVA gels in the region of high melting temperatures (above 60°C). ΔH of the s-PVA gels was higher than that of the a-PVA gels at same saccharose contents. ΔH of the a-PVA gels with saccharose contents above 50 wt % was nearly equal to or lower than that of the s-PVA hydrogels.[14-16] However, the melting temperature was above 100°C for a-PVA gels (over $C = 6$ g/dL) with saccharose contents of 60 wt %.

Dynamic Modulus of Gels

Tables I and II show the dynamic compressive modulus of a-PVA hydrogels with or without saccharose (50 or 0 wt %) obtained after three cycles of the freezing/thawing process. Both gels were roughly transparent but the modulus of the gel with saccharose was higher than that of the gel without saccharose. The gel without saccharose was partially unstable. As both gels were dried under freezing, the gel with saccharose became translucent but its volume scarcely changed (Table I); therefore, the mod-

Table II   Dynamic Compressive Modulus of a-PVA Hydrogels With or Without Saccharose from 25°C to 50°C and Transparency of Gels. (Initial Saccharose Content: 50 and 0 wt %; Initial Polymer Concentration: 5 g/dL.)

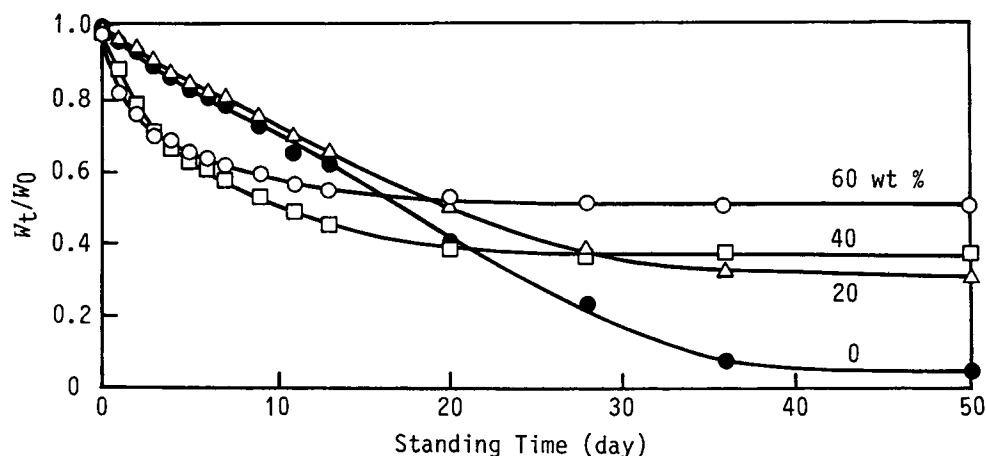|	Gels with Saccharose	Gels without Saccharose
(a) As-frozen/thawed gels	40 kPa	30 kPa
	Transparent	Transparent
(d) Gels of (a) preserved in water	30 kPa	13 kPa
	Transparent	Transparent
(e) Freeze-dried gels of (d)	1.6–1.2 MPa	3 MPa
	Chalky	Chalky

Figure 6 Change in weight of gels in air during standing at room temperature for 5 g/
dL a-PVA (DP = 2400) gels. Numerals in figure are saccharose contents.

ulus increased only a very little. However, all water molecules in the gel without saccharose were released by freeze-drying, the dry gel became porous and chalky, and the modulus increased drastically.

As the as-frozen/thawed gels were preserved in water for 24 h, the modulus of the gel decreased somewhat (Table II). Namely, many weak, unstable junctions in the gel dissolved. However, the gel without saccharose preserved in water was, as a whole, stable in comparison with that of the as-frozen/thawed gel without saccharose. It is considered that the stable junctions were reformed after dissolving the weak, unstable junctions. During re-freeze-drying of the gel, the mechanically stable junctions increased and the modulus rose to 3 MPa.

Syneresis of Gels

Figure 6 shows the relations between W_t/W_0 and the standing time for 5 g/dL a–PVA gels. W_0 is the weight of gels after three cycles of freezing/thawing and W_t is that of gels after standing in air for t days. W_t/W_0 decreased rapidly with an increase in the standing time for the gels with saccharose contents of 40–60 wt % and it gradually approached the fixed value after standing for 20 days. W_t/W_0 decreased slowly with an increase in the standing time for gels with saccharose contents of 0–20 wt % and reached the constant values after standing for 50 days. In the saccharose/water gels which came to equilibrium, the inside was flexible whereas the outside was rigid. The a-PVA hydrogel released almost all water molecules after standing for 50 days. An example of gels with and without saccharose after standing for 50 days is shown in Figure 7 (initial polymer concentration: 10 g/dL).

Table III shows the effect of the initial polymer concentration of the volume reduction of gels after standing for 50 days in air. W_{50}/W_0 of 10 g/dL a-PVA gels is higher than that of 5 g/dL a-PVA gels. Namely, the volume reduction of gels in air can suppress at high initial polymer and saccharose contents. W_{50}/W_0 was ca. 0.3 for a-PVA gels with saccharose contents of 20 wt % after standing for 50 days. The value was higher than that of ca. 0.25 obtained only when all water was released from the gel; that is, the gel holds tightly a small amount of water after standing for 50 days. Though the gel without saccharose was rigid after standing for 50 days, the gels with saccharose were still flexible. Saccharose transuded from the latter gels with the vaporization and syneresis of water. The decrease rate of W_t/W_0 with standing was low for the gels with high polymer concentration and the time taken

Figure 7 Photograph of gels with or without saccharose after standing for 50 days in air (initial polymer concentration: 10 g/dL).

Table III W_{50}/W_0 **Values of a-PVA Hydrogels with Initial Polymer Concentrations of 5 g/dL and 10 g/dL[a]**

5 g/dL a-PVA Gels		10 g/dL a-PVA Gels	
Initial Saccharose Content (Wt %)	W_{50}/W_0	Initial Saccharose Content (Wt %)	W_{50}/W_0
60	0.51 (10.7)[b]	60	0.64 (6.5)
40	0.37 (7.9)	40	0.42 (4.2)
20	0.30 (6.4)	20	0.34 (3.4)
0	0.047 (1.0)	0	0.099 (1.0)

[a] W_{50} is the weight of gels after standing for 50 days at room temperature in air.
[b] Numerals in brackets are ratio of W_{50} to weight of residual a-PVA.

until equilibrium was large. Though the similar results were also obtained for the s-PVA gels, the release rate was higher than that of a-PVA gels (Fig. 8).

In the case of 5 g/dL a-PVA gels, the mass ratio of the equilibrium gels to the residual PVA was 10.7, 7.9, and 6.4 for the gels with saccharose contents of 60, 40, and 20 wt %, respectively. In the case of 10 g/dL a-PVA gels, the ratio was 6.5, 4.2, and 3.4 for the gels with saccharose contents of 60, 40, and 20 wt %, respectively. Though the mass ratio for the 5 g/dL a-PVA gels was larger than that for the 10 g/dL a-PVA gels at the same initial saccharose contents, the mass of the equilibrium gels for the former was lower than that for the latter. Namely, the volume change of gels during standing in air was smaller in the case of the gels with higher polymer concentration and saccharose content.

The PVA hydrogels with lower saccharose contents occasionally became musty on the surface by standing in air for a long time. The standing in an atmosphere of formalin was advantageous to prevent this mustiness.

Thermal Analysis of Gels

A part of water in gel vaporized in air and transuded with saccharose by syneresis on the gel surface. The latter solutions were wiped off by filter paper. As saccharose released with water from the initial standing, even the mass could not be qualitatively determined. The inside of gels (named equilibrium gels) that reached the equilibrium W_t/W_0 value was flexible and the outside was somewhat rigid. The mass of equilibrium gels decreased scarcely under vacuum even at 100°C. The gels colored brown at 100°C.

Figure 9 shows the DSC thermographs for the outside of equilibrium a-PVA gels ($C = 5$ g/dL). The peak at 220°–230°C corresponds to the melting of PVA and the peak at 140°–180°C corresponds to the melting of saccharose. The peak that correspon-
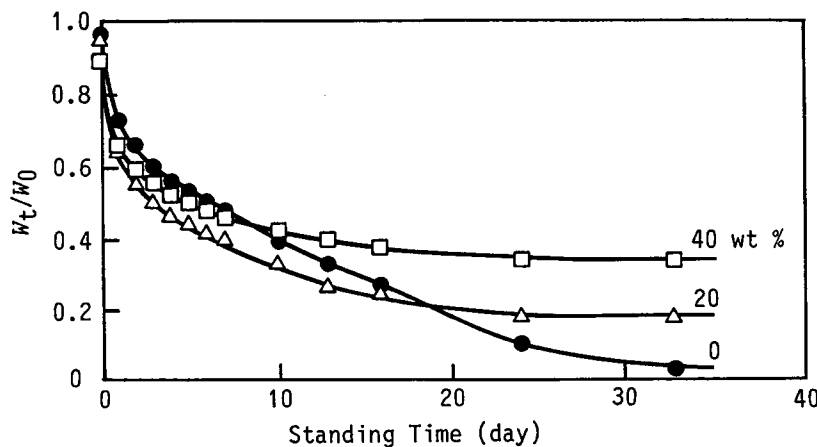

Figure 8 Change in weight of gels in air during standing at room temperature for 2 g/dL s-PVA gels. Numerals in figure are saccharose contents.

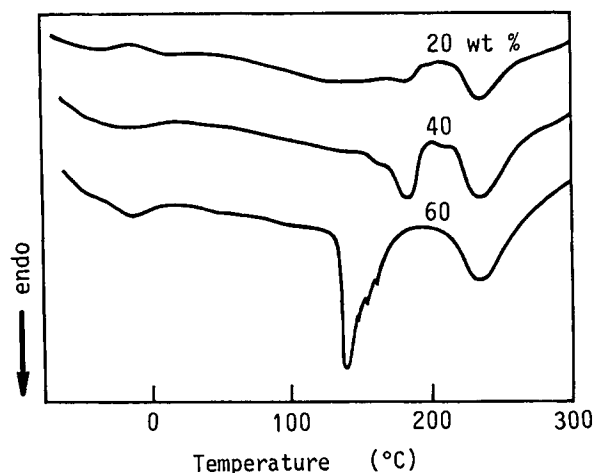**Figure 9** Differential scanning thermographs of equilibrium 5 g/dL a-PVA (DP = 2400) gels at a heating rate of 20°C/min. Numerals in figure are saccharose contents.

ded to the melting of saccharose lowered to ca. 140°C with an increase in the saccharose content. The hydrated saccharose that is present in the outside of equilibrium a-PVA gels with saccharose contents of 60 wt % is much more than that for gels with saccharose contents of 40 wt %. Therefore, the surface of the former gels was sticky.

Though the peak temperature of PVA increased with an increase in the heating rate in DSC from 226°C to 236°C (saccharose content: 60 wt %) or from 224°C to 237°C (40 wt %), the peak temperature of saccharose lowered from 158°C to 138°C (60 wt %) or from 184°C to 182°C (40 wt %). The slow heating rate supports the vaporization of water that hydrates tightly to saccharose. The melting curves were broad in the region of high temperature for gels with saccharose contents of 60 wt % and in the region of the low temperature for gels with saccharose contents of 40 wt %. The results also support the vaporization of water that hydrate tightly to saccharose. For the inside of gels with saccharose contents of 60 wt %, the melting curves that correspond to hydrated saccharose were also broad in the region of low temperature. The results are considered to imply the vaporization of water that hydrates weakly to saccharose.

In the DSC curves of equilibrium gels, the glass transition (low saccharose contents) and the melting of water ice (high saccharose contents) were sometimes recognized at ca. 60°C and −17°C, respectively.

In the case of the as-frozen/thawed a-PVA gels shown in Tables I and II, the peak temperatures in DSC curves are influenced by the content of sac-

charose. In Table I, the gels of (b) with and without saccharose have peak temperatures corresponding to a-PVA at 234.9°C and 236.3°C, respectively. The former gel has a peak temperature corresponding to hydrated saccharose at 130°–180°C. In Table II, the gels of (e) have peak temperatures of 234.9°C and 238.7°C, respectively. The former gel does not have the peak temperature corresponding to saccharose. The saccharose in the gel of (b) dissolved perfectly into water. Therefore, the modulus of the freeze-drying gel increased drastically. However, the peak temperature was equal to that of the gel of (b) and the structure in the gel of (b) is memorized even in the gel of (e). In the case of gels without saccharose, the peak temperature of the dry gel of (e) increased to 238.7°C. During the standing of the gel of (b) in water, namely, thermally stable junctions are formed.

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