

Properties of Syndiotactic-Rich Poly(vinyl Alcohol) Thin Film in Water. VII. Elastic Behavior of Swollen Film in Water through Heating / Cooling or Cooling / Heating Cycles

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Synopsis

The thermoelastic behavior for highly swollen films of syndiotactic-rich poly(vinyl alcohol) (*s*-PVA) was ascertained under loads in water through heating/cooling or cooling/heating cycles (in the range of 25–70°C). The *s*-PVA films kept at the high temperature of 70°C behaved as a perfect elastomer through the cooling/heating cycle and had very low Young's modulus, $2\text{--}3.5 \times 10^6$ dyn/cm². When highly swollen *s*-PVA films were kept at lower temperatures below about 50°C for a long time, microcrystals were formed or propagated in the *s*-PVA films and plastic deformation occurred in addition to elastic deformation through heating process. The microcrystalline growth and propagation at lower temperatures were supported by an increase in Young's modulus and a decrease in the molecular weight between junctions.

INTRODUCTION

The authors¹⁻⁶ have reported that thin films of syndiotactic-rich poly(vinyl alcohol) (*s*-PVA) had high water resistance and behaved as an elastomer in water at high temperatures. However, even highly swollen *s*-PVA films exhibited plastic deformation in addition to elastic deformation.^{4,6} The plastic deformation was remarkable for films under the high elongation.^{4,6}

In this paper, the conditions in which highly swollen *s*-PVA films exhibited perfect elastic behavior were studied by heating/cooling cycles, and the elasticity was ascertained by the use of rubber elastic theory.

EXPERIMENTAL

Sample and Films

An *s*-PVA derived from vinyl trifluoroacetate was used as a sample. The degree of polymerization and the content of syndiotactic diad were 1670 and 55.2%, respectively. The *s*-PVA films (70 × 150 mm) were made by casting an aqueous solution at room temperature on a glass plate. The thickness of the films was about 0.062 mm. The films were cut to a width of about 2 mm (length = 70 mm).

Forced Elongation and Contraction

The untreated tapelike *s*-PVA films were fixed on a hand-drawing machine. The forced elongation and contraction of the films in water were performed at 70°C by the same method described in our previous papers.^{4,6}

Elastic Behavior under Constant Loads

The untreated tapelike *s*-PVA films were swollen in water at 70°C for 1 h followed by preservation in water at room temperature. Before the measurement of film length under constant loads, the film was kept in water of 25 or 70°C until equilibrium swelling, that is, the state at which no further elongation occurred and then a weight was hung. After the film length reached an equilibrium value, the film length was measured with the same method described in our previous papers^{1-3,5} under heating/cooling or cooling/heating cycles. The heating and cooling rates were 0.5°C/min.

RESULTS AND DISCUSSION

Forced Elongation and Contraction

Figure 1 shows the change in film length for untreated *s*-PVA film with the original thickness of 0.062 mm in water by forced, repeated elongation and contraction. It was analogous to the result for the untreated *s*-PVA film with

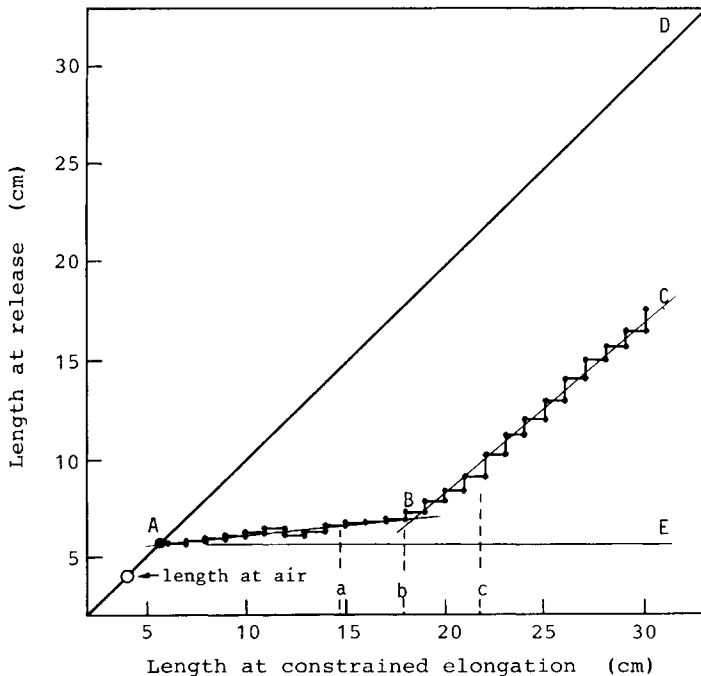


Fig. 1. Relation between the film length at release and the film length at constrained elongation in water at 70°C for untreated *s*-PVA film: (A) equilibrium-swelling length at 70°C before drawing; (B) transition point from ideal elastic deformation to remarkable plastic deformation.

TABLE I
Film Lengths Obtained under Each Condition

Expt no.	Load under constrained drawing, w (g)	Original length l_0 (cm) ^c	ESFL ^d without load at 70°C, l_{S25} (cm) ^e	ESFL under load of w (g) at 25°C, l_e cm	ESFL without load before heating (from 25°C)/cooling (from 70°C) cycles				
					l_1 (cm)	l_2 (cm)	l_3 (cm)	l_4 (cm)	l_5 (cm)
1	5	1	1.29	3.68	Start 1.94	1.92	2.01	2.10	End 2.14
2	10	1	1.29	4.49	Start 2.72	2.68	2.79	2.82	End 2.84
3	20	1	1.30	5.43	Start 3.93	3.90	3.91	4.00	End 4.00
4	20 ^b	1	1.33	4.48	Start 3.65	3.76	3.85	3.93	End 4.01
5	5	1	1.32	—	—	—	1.79	—	—
6	5	1	1.28	—	End 2.01	2.02	2.02	1.99	Start 1.71
7 ^a	5	1	1.31	—	End 1.66	1.67	1.66	1.63	Start 1.58

^aThe cycle for expt. no. 7 was first initiated from 70°C through the cooling process and the cycle for expt. nos. 1-6 was first initiated from 25°C through the heating process.

^bThe film was drawn by a force of $w = 20$ g until the length reached by a static load of $w = 10$ g.

^cThe films with lengths of $l_d = 2.64-4.29$ cm were actually used, but in order to compare with the unprocessed length and the equilibrium swelling film lengths l_d was normalized as $l_0 = 1$ cm.

^dESFL = equilibrium swelling film length.

^eFilms were first swollen in water at 70°C, and then the swollen film was kept at 25°C.

the original thickness of 0.017 mm shown in a previous paper,⁴ that is, it was independent of film thickness. The length of the former film changed from original length $l_d = 4.0$ cm to the film length $l_s = 5.7$ cm after equilibrium swelling in water at 70°C ($l_s/l_d = 1.43$) and the length of the latter film changed from $l_d = 4.0$ cm to $l_s = 6.05$ cm ($l_s/l_d = 1.51$). In Figure 1, lines AE and AD show ideal elastic deformation and ideal plastic deformation, respectively. In the low elongation region AB, elastic deformation occurs chiefly with a slight plastic deformation. In the high elongation region BC, plastic deformation occurs chiefly with a slight elastic deformation. In the latter region, the elastic deformation increases slowly with an increase in the plastic deformation, adding to a constant elastic deformation at the transition point B. Therefore, the next section heating/cooling cycles were performed in the region AB and BC, and at B.

Elastic Behavior under Constant Loads

Table I shows the film lengths obtained under each condition. In this experiment, the s-PVA films with the original lengths of $l_d = 2.7$ – 4.3 cm were used. In order to compare with l_d and the lengths obtained under other conditions, l_d was normalized as $l_0 = 1$ cm. l_{S25} is the equilibrium length at 25°C after original films were first swollen in water 70°C. l_s/l_d was about 1.43, but l_{S25}/l_d was about 1.3. The latter value is equal to that for films swollen at 55–60°C, that is, the films swollen at higher temperatures were contracted by the preservation for a long time at lower temperatures. l_e is the equilibrium length at which the swollen films with length of l_{S25} were loaded at 70°C by weights $w(g)$. Each l_e obtained for the experiment numbers (expt. nos.) 1, 2, and 3 corresponds to film lengths at a, b, and c points shown in Figure 1, respectively. The weights $w(g)$ were loaded in order to eliminate the plastic deformation region recognized in Figure 1. The film of expt no. 4 was drawn instantaneously by a force of $w = 20$ g up to the length reached by a static load of $w = 10$ g. The films drawn to l_e were kept in water at room temperature and were used for the experiment of heating/cooling or cooling/heating cycles. l_1 – l_5 values shown in Table I are the equilibrium swollen lengths at 25 or 70°C without load. Since then the experiments of heating/cooling or cooling/heating cycles were performed after the equilibrium swelling under loads of 1–5 g at 25 or 70°C was reached.

Figures 2–5 show the relations between the draw ratio and the temperature for expt. no. 1–4, respectively. The draw ratio was estimated by the following equation:

$$\text{draw ratio} = \frac{\text{film length through cycles under a load}}{l_1, l_2, l_3, l_4, \text{ or } l_5}$$

All the expt. nos. 1–4 were first performed under a load of 1 g with heating/cooling cycle. Before cycling, films were reserved in water overnight at room temperature without load and then the experiments were repeated in turn under loads of 2–5 g. The draw ratios for all the experiments shown in Figures 2–4 increased with heating except that for a load of 1 g for expt. no. 3 (Fig. 4), that is, plastic deformation occurs through heating process. However,

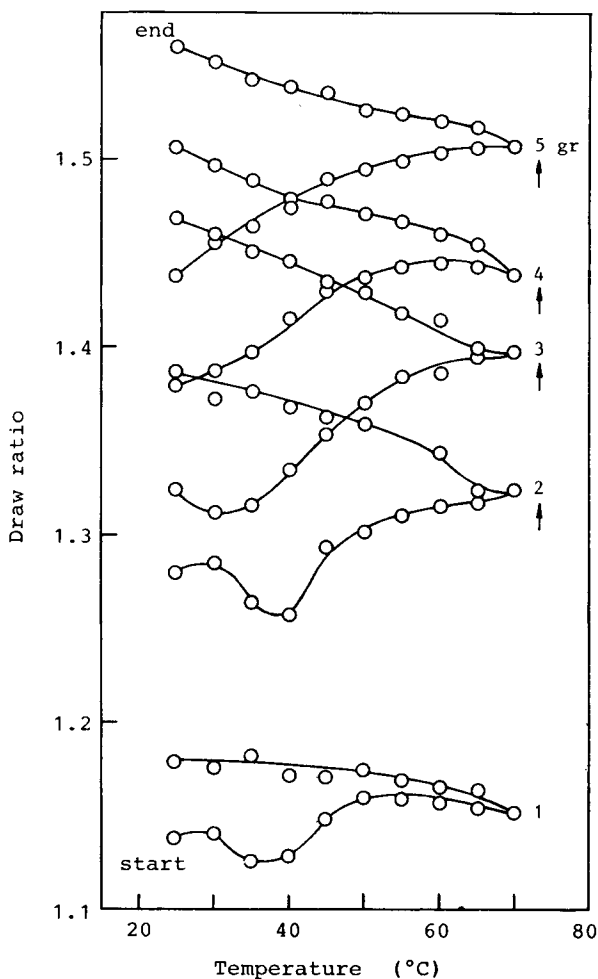


Fig. 2. Changes in the draw ratio of the swollen *s*-PVA film under loads (1–5 g) through the heating/cooling cycle for expt. no. 1.

the draw ratios increased during cooling process, that is, elastic deformation occurs. In the case of expt. no. 3, as the value l_e is very high in comparison with others, microcrystals that were broken during heating under low load ($w = 1$ g) are considered not to exist. In the case of expt. no. 4, the swollen film was drawn instantaneously under a high force of $w = 20$ g up to the length $l_e = 4.5$ cm shown in expt. no. 2. l_1 in this case was higher than that in expt. no. 2 and was nearly equal to that in expt. no. 3, that is, the abrupt loading to the swollen film prefers the rupture of microcrystalline junctions to the uncoiling of the entanglement of polymer chains. In the case of expt. nos. 1–3, the heating process under load of 1 g (1 and 2 g for expt. no. 3) gives only weak effect to plastic deformation. In Figure 2, the draw ratio is smallest at 30–40°C during heating process. Such a result is consistent with that for the changes in the bending⁷ or shear moduli⁸ of aqueous *s*-PVA gels prepared at low temperature with an increase in temperature. The result obtained in this

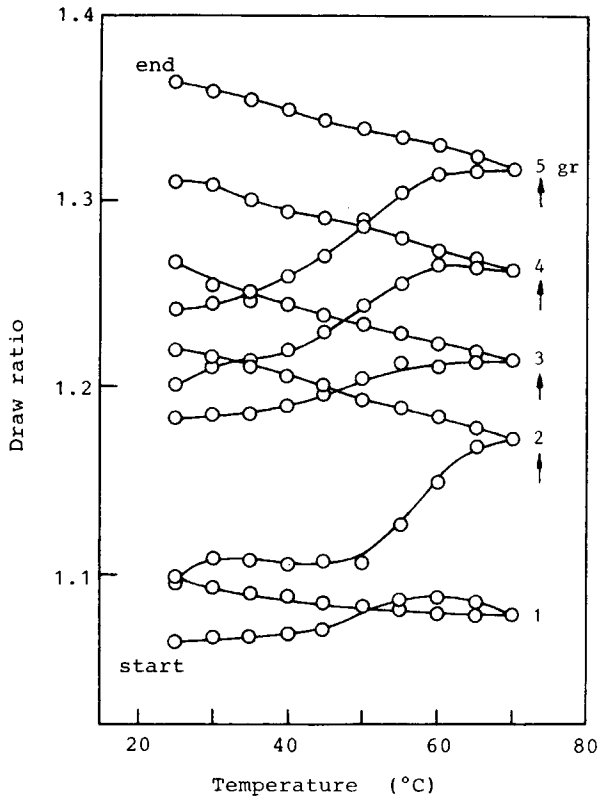


Fig. 3. Changes in the draw ratio of the swollen s-PVA film under loads (1-5 g) through the heating/cooling cycle for expt. no. 2.

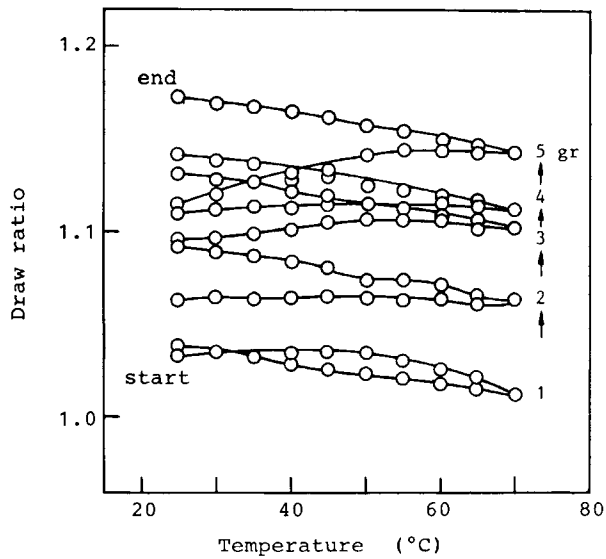


Fig. 4. Changes in the draw ratio of the swollen s-PVA film under loads (1-5 g) through the heating/cooling cycle for expt. no. 3.

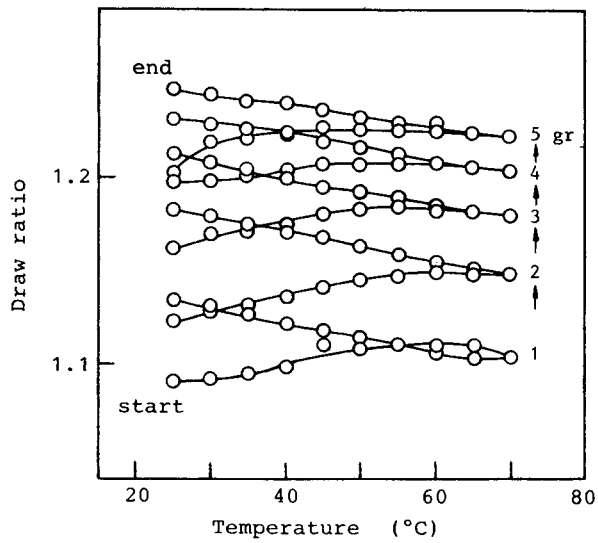


Fig. 5. Changes in the draw ratio of the swollen *s*-PVA film under loads (1-5 g) through the heating/cooling cycle for expt. no. 4.

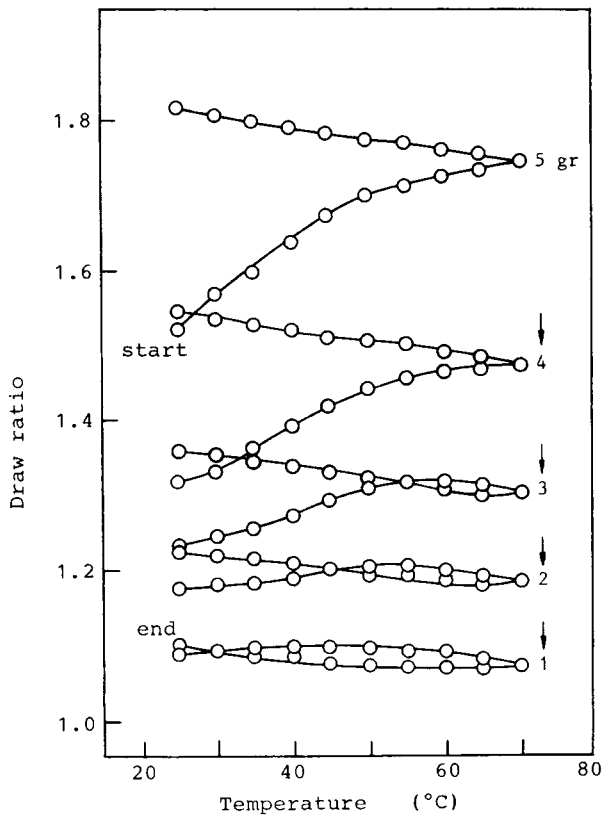


Fig. 6. Changes in the draw ratio of the swollen *s*-PVA film under loads (5-1 g) through the heating/cooling cycle for expt. no. 6.

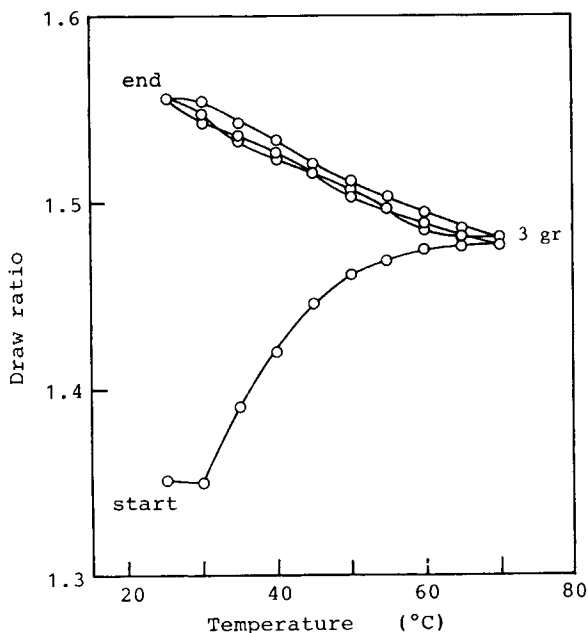


Fig. 7. Changes in the draw ratio of the swollen *s*-PVA film under a load (3 g) through two heating/cooling cycles for expt. no. 5.

experiment also supports the initiation and propagation of microcrystals in film preserving water even under lower load in the neighborhood of 30–40°C.

Figure 6 shows the relations between the draw ratio and the temperature for expt. no. 6 in which the experiment was initiated first from a load of 5 g at heating/cooling cycle contrary to expt. no. 1 (first from a load of 1 g). The increase in draw ratio for the former through heating process is not remarkable in comparison with that for the latter, especially under loads of 1 and 2 g. Figure 7 shows the relation between the draw ratio and the temperature for expt. no. 5. Expt. no. 5 is the result that was performed at two heating/cooling cycles under load of 3 g. The draw ratio increased with the increase in temperature at first cycle and decreased at second cycle. Namely, the swollen films exhibit plastic deformation behavior at first cycle and elastic deformation behavior at second cycle through heating process. The draw ratio shown in Figures 2–7 increases with lowering of temperature; thus in Figure 8 the cycles were first initiated from 70°C through cooling process. In any case, elastic deformation was recognized.

If swollen films behave elastically, it is expected that the swollen films contract under constant loads or elasticity increases under fixed length through heating process. Figures 9 and 10 show the relations between the elasticity and the temperature for expt. nos. 5 and 7, respectively. In our previous paper,⁵ the volume of swollen films was determined by postulating an isotropic swelling, and Young's modulus of the film swollen in water at 70°C was reported to be 1.6×10^6 dyn/cm². In this paper, the degrees of swelling in three directions (dry state: $40 \times 2.0 \times 0.06$ mm) were measured and the anisotropic swelling (swelling state: $51 \times 2.6 \times 0.13$ mm) was found. Both the

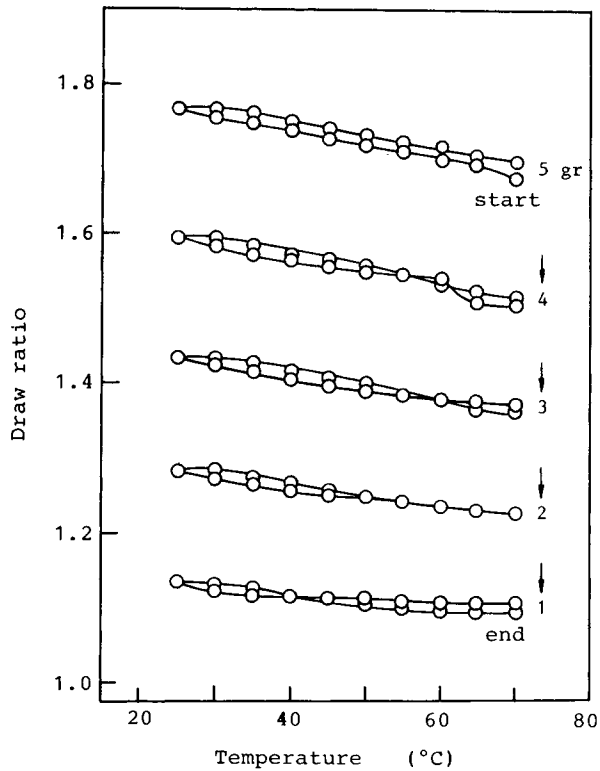


Fig. 8. Changes in the draw ratio of the swollen *s*-PVA film under loads (5-1 g) through the cooling/heating cycle for expt. no. 7.

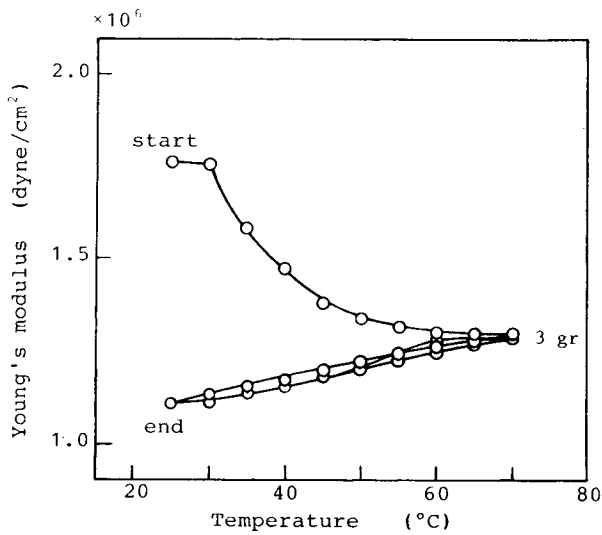


Fig. 9. Relation between the elasticity and the temperature for the swollen *s*-PVA film of expt. no. 5.

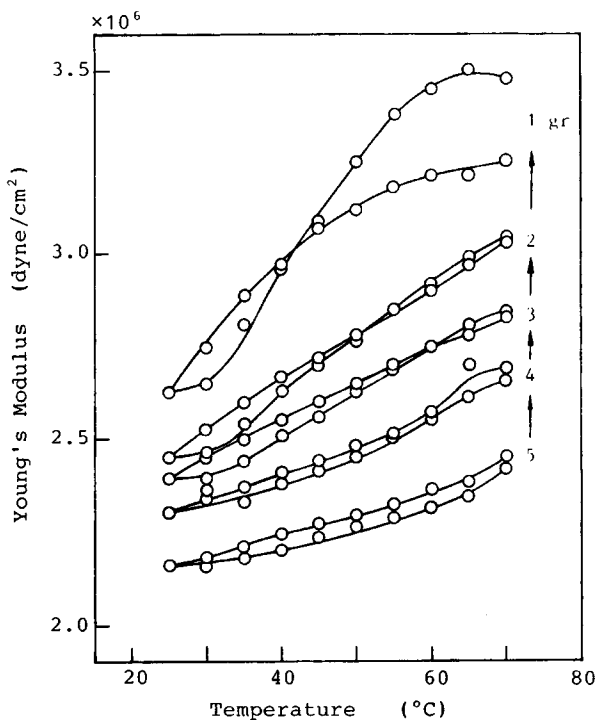


Fig. 10. Relations between the elasticity and the temperature for the swollen *s*-PVA film of expt. no. 7.

degrees of swelling to length and width directions were almost the same, but the degree of swelling in the thickness direction was about two times that of the other directions. In this paper, the ratio of the cross section of swollen film to that of original film $A_s/A_d = 2.82$ was used in order to estimate the elasticity of swollen films by postulating that the volume of the films does not change during heating/cooling cycles. Figures 9 and 10 show the relations between Young's modulus and the temperature for expt. nos. 5 and 7. The swollen films behave elastically except the heating process of first cycle for expt. no. 5 as shown in Figures 9 and 10. The molecular weight between junctions M_c was estimated in the same way as our previous paper⁴ by the following equation:

$$M_c = \frac{1}{\epsilon v v_2^{2/3} / 3RT + 2/M}$$

where ϵ is Young's modulus, v the specific volume of polymer, v_2 the volume fraction of polymer in swollen film, R the gas constant, T the absolute temperature, and M the molecular weight of unprocessed polymer. M_c for expt. no. 6 and the first cycle of expt. no. 5 increased with the elevation of temperature, but the increase was slight as shown in Figure 11. Moreover, M_c was constant through cooling/heating cycle for expt. no. 7 and through

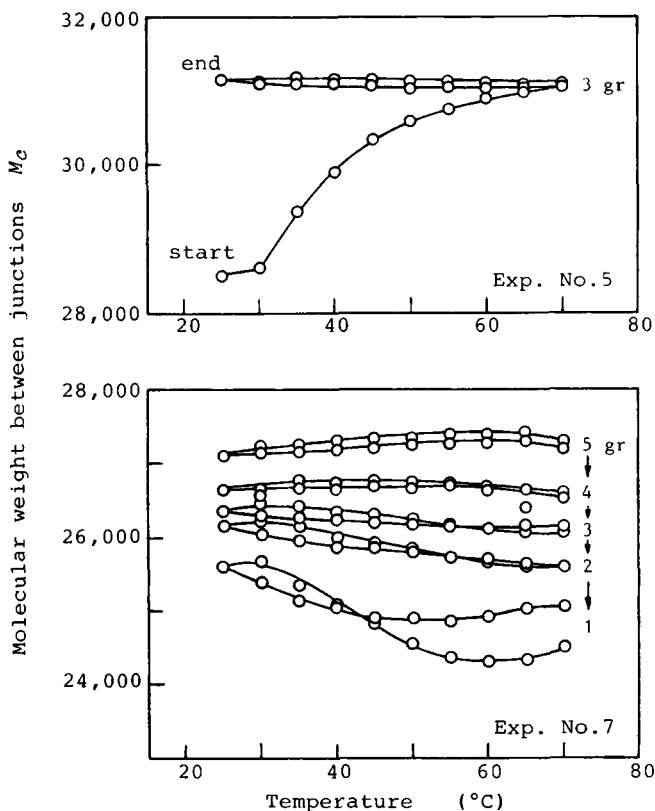


Fig. 11. Relations between the molecular weight between junctions in the swollen *s*-PVA film and the temperature for expt. nos. 5 and 7.

cooling cycles for expt. nos. 5 and 6. This fact supports that the swollen films behave elastically.

Sakurada et al.⁹ and Shibatani¹⁰ have investigated the effect of the stereoregularity on the thermoelastic behavior for the swollen PVA film crosslinked lightly by irradiation. Shibatani¹⁰ has reported that crosslinking loci in PVA chains were syndiotactic sequences of different lengths and that the number of network chains formed by gelation for the swollen PVA films in water increased with an increase in temperature. In this paper, the number of network chains and the length of network microcrystals were estimated by the same method shown by Shibatani,¹⁰ but the molecular weight between junctions M_c decreased with the elevation of temperature for expt. no. 7. This result does not correspond to that of Figures 8, 10, and 11.

CONCLUSION

The thermoelastic behavior of highly swollen *s*-PVA film was ascertained by heating/cooling or cooling/heating cycles in water. The films exhibit plastic deformation in addition to elastic deformation in water during heating, whereas the films behaved as a perfect elastomer during cooling. The elastic character was lost by subjecting film for a long time at low temperature, that

is, the preservation at low temperature is considered to propagate and produce microcrystals. In order to avoid the propagation and production of microcrystals during heating/cooling cycles, swollen films should be kept at temperatures above 50°C, and the cooling/heating cycle initiated from high temperatures.

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