Studies on the temperature dependence of the elastic modulus of crystalline regions of polymers: 14. Poly(vinyl alcohol) with different tacticities*

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The temperature dependence of the elastic modulus E_l of crystalline regions in the direction parallel to the chain axis has been measured by X-ray diffraction for poly(vinyl alcohol) (PVA) with different tacticities. The E_l value for PVA with 55.4% syndiotactic diads, sPVA(55.4%), decreased above 120°C, which was in accordance with that of atactic PVA. The lattice spacing for the (0 2 0) plane (the fibre axis is b) also decreased with increasing temperature. The thermal expansion coefficient α_c changed discontinuously around the temperature range where E_l began to decrease. These phenomena could be explained using the kinked-chain model, where a small amount of a contracted portion, such as a kink, was incorporated into the chain molecule as in the case of atactic PVA. On the other hand, the E_l value of sPVA(63.0%) remained unchanged till 150°C. The value of α_c did not change with increasing temperature in this case. Consequently, the molecular motion that is responsible for the decrement of E_l is considered to be restricted for sPVA(63.0%) because of strong intermolecular hydrogen bonds. Further, increasing the syndiotacticity is considered to be one of the most effective ways to introduce high heat resistance into PVA.

(Keywords: crystal modulus; poly(vinyl alcohol); tacticity; temperature dependence; elastic modulus; mechanical properties)

INTRODUCTION

The elastic modulus E_l of crystalline regions of polymers in the direction parallel to the chain axis provides important information on the molecular conformation and on the relation of this to the mechanical properties of polymers[1–5]. We have been measuring the elastic modulus E_l by X-ray diffraction and were able to relate its value, viz. the extensivity and the deformation mechanism of a polymer molecule, to the molecular conformation in the crystal lattice[1–5]. The value of E_l for polymers with a fully extended planar zig-zag conformation, i.e. polyethylene (PE) and poly(vinyl alcohol) (PVA), is found to be 235 and 250 GPa, respectively. In these cases, the chain deforms through bond stretching and bond angle bending, which have relatively high force constants. Knowledge of E_l is of interest from the mechanical point of view, because it gives us the maximum value for the specimen modulus of a polymer. Values of E_l for PE and PVA are the highest among the flexible polymers. Thus, this is the reason why high modulus is achieved for PE. Nowadays, much effort has been expended in getting molecular extension for PVA, using the E_l value as a measure of practical success in a process aimed at obtaining high-modulus oriented polymers[6–9]. On the other hand, the values of E_l for polymers with contracted or helical conformation are smaller because these chains deform mainly through a change in the internal rotation angle whose force constant is small.

We have also investigated the temperature dependence of E_l for many polymers and discussed them in terms of the thermal expansivity and stability of the crystalline regions of each polymer[5]. In many cases, including atactic PVA[10], the E_l value decreased above a certain temperature. Further, in the course of these studies, we found that the temperature dependence of E_l differed for some polymers, for example PE[11] and polyoxymethylene[12], despite the fact that they are chemically the same polymers. In the case of PVA, a lot of properties are known to change depending on its tacticity[13,14].

In this study, we measured the temperature dependence of E_l for PVA with different tacticities at high temperature, and investigated the molecular motions in the crystalline regions.

EXPERIMENTAL

Samples

Two kinds of PVA with different diad syndiotacticities (55.2% and 63.0%) were used in this study. In order to

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Table 1 Conditions of sample preparation for various poly(vinyl alcohols)

	sPVA(55.2%)	sPVA(63.0%)
Drawing		
temperature (°C)	160	200
ratio	8.0	6.0
Annealing		
temperature (°C)	190	200
time (min)	30	30

obtain syndiotactic PVA, vinyl trifluoroacetate (VTFA) was polymerized in bulk or in solution[15]. The poly(vinyl trifluoroacetate) thus obtained was converted to PVA by ammonolysis with diethylenetriamine.

The syndiotactic diad content of PVA was measured by the optical density D ratio of the infra-red absorption bands at 916 and 849 cm^{-1} via the relation[16]:

$$\text{Syndiotactic diad} = 72.4(D_{916}/D_{849})^{0.43}$$

Infra-red measurements were made on a Shimadzu FT-IR 4200 infra-red spectrophotometer.

To obtain sPVA(55.2%), bulk polymerization was carried out at 60°C with the use of benzoyl peroxide as initiator.

To obtain sPVA(63.0%), solution photopolymerization of VTFA in 20 vol% pentane was conducted at −78°C for 108 h by ultra-violet light employing 2,2′-azobis(2,4-dimethylvaleronitrile) as a sensitizer. The degree of polymerization was 1590.

PVA was dissolved in water at 130°C, and cast from a 5% solution.

Table 1 shows the drawing and annealing conditions of PVA with different tacticities. Though we tried to unify the conditions of preparation of oriented samples, the drawing condition was very critical and it was difficult to draw a highly syndiotactic PVA.

Specimen modulus

The macroscopic specimen modulus was measured from the initial slope of the stress–strain curve by using a tensile tester (Shimadzu, Autograph SD-100) at 25°C. The initial length of the specimen was 20 mm and the extension rate was 20 mm min^{-1}.

Crystallite size

The observed profile for the meridional 0 2 0 reflection was corrected for both instrumental and Cu Kα doublet broadening. Finally, the crystallite size $D_{(020)}$ along the chain axis was estimated by using Scherrer's equation:

$$D_{(020)} = \lambda/\beta \cos\theta$$

where λ is the X-ray wavelength, θ is the Bragg angle of the reflection and β is the pure integral width of the reflection.

Density and degree of crystallinity

The density of the specimen was obtained by a flotation method (benzene–carbon tetrachloride) at 30°C. The degree of crystallinity was calculated by the following equation:

$$1/d = C_c/d_c + (1 - X_c)/d_a$$

where d_c is the crystal density (1.345 g cm^{-3})[17] and d_a is the amorphous density (1.269 g cm^{-3})[18].

Melting point and heat of fusion

The melting point T_m and the heat of fusion ΔH were measured by using a differential scanning calorimeter (Daini Seikosha, SSC-560S) with a sample of weight 10 mg and at a heating rate of 10°C min^{-1}. Values of T_m and ΔH were determined as peak temperature and area of the melting peak, respectively. Sn was used as standard sample.

Degree of orientation

The degree of orientation π was defined by:

$$\pi = (180 - H^\circ)/180$$

where H° is the half-width of the intensity distribution curve for the 0 2 0 reflection of PVA along the Debye–Scherrer ring.

Measurement of the elastic modulus E$_l$ *of crystalline regions*

The elastic modulus E_l of crystalline regions was measured by means of an X-ray diffractometer (Rigaku Denki RAD-B system) equipped with both a stretching device and a load cell. E_l at high temperature was measured with the electric heating cell through a temperature controller. The temperature was detected with a thermocouple, and it could be maintained within an accuracy of ±1°C during the measurements.

The diffraction profile for the (0 2 0) plane of PVA (fibre axis is b) was measured by the symmetric transmission method using Cu Kα radiation. The change of the (0 2 0) spacing induced by constant stress was measured by the shift of peak position.

The strain ε in the crystalline regions was estimated by use of the relation:

$$\varepsilon = \Delta d/d_0$$

where d_0 denotes the initial lattice spacing and Δd is the change in lattice spacing induced by constant stress. The experimental error in measuring the peak shift was evaluated ordinarily to be less than ±0.5°/100° in an angle 2θ.

In order to know the real stress that is causing the lattice extension in the crystalline regions, it has simply been assumed that the stress is homogeneous throughout the measurement, and that there is continuity of stress in all samples. That is, the stress σ_c in the crystalline regions was assumed to be equal to the stress σ applied to the sample. In order to obtain experimental support for this assumption, we have carried out measurements by using several specimens of the same polymer with different microstructures and methods of preparation, to give, as would be expected from the assumption, an inherent value of E_l. As was previously reported, this assumption has been proven experimentally for PVA[2], PE[2,3,5,19], poly(ethylene terephthalate) (PET)[20], cellulose[21], poly(p-phenylene terephthalamide)[22], isotactic poly(4-methyl-1-pentene) (P4M1P)[23], etc.

Values of σ and ε were not corrected for the inclination of the lattice plane, because we use the meriodional 0 2 0 reflection in this study.

In this way, E_l could be calculated by use of the following equation:

$$E_l = \sigma/\varepsilon$$

A more detailed description of the measurement was given in earlier papers[1–5,10–12,19–23].

RESULTS AND DISCUSSION

Characterization of PVA with different tacticities

Figure 1 shows the X-ray fibre photographs of sPVA at room temperature. It showed high crystallinity and a high degree of orientation of the crystallites.

Table 2 shows some characteristics of sPVA along with those of atactic PVA (commercial fibre (Unitika Ltd) was annealed at 180°C for 30 min under constant length) previously reported[10]. The sPVA samples showed relatively high specimen modulus considering their low draw ratios. Both the specimen modulus and the degree of crystallite orientation for sPVA(55.2%) were higher than those of sPVA(63.0%) and depended on their difference in draw ratio.

Temperature dependence of E_l *of syndiotactic PVA*

Figure 2 shows the stress–strain (σ–ε) curves for the (0 2 0) plane of sPVA(55.2%) at various temperatures. The lattice extensions were always reversible. The σ–ε curves below 99°C could be expressed as a straight line through zero, but those at 126°C and 150°C had different slopes. These differences exceed the experimental error,

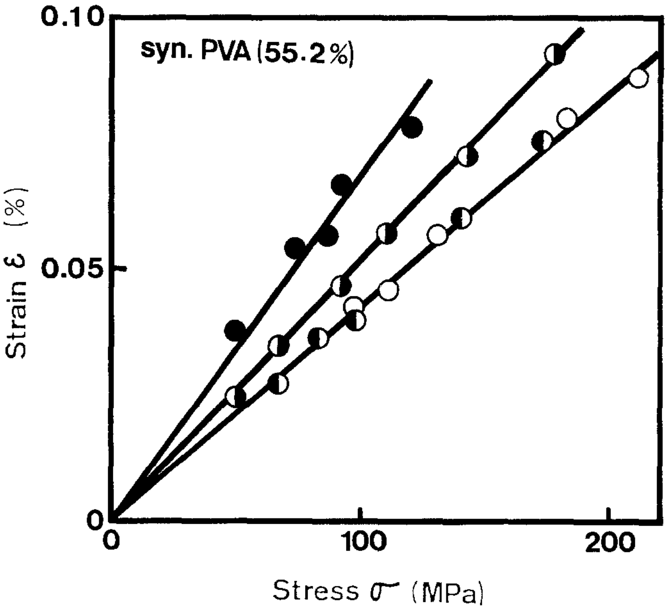

Figure 2 Stress–strain curves for the (0 2 0) plane of sPVA(55.2%) at various temperatures: (○) 20°C, (◐) 99°C, (◑) 126°C, (●) 150°C

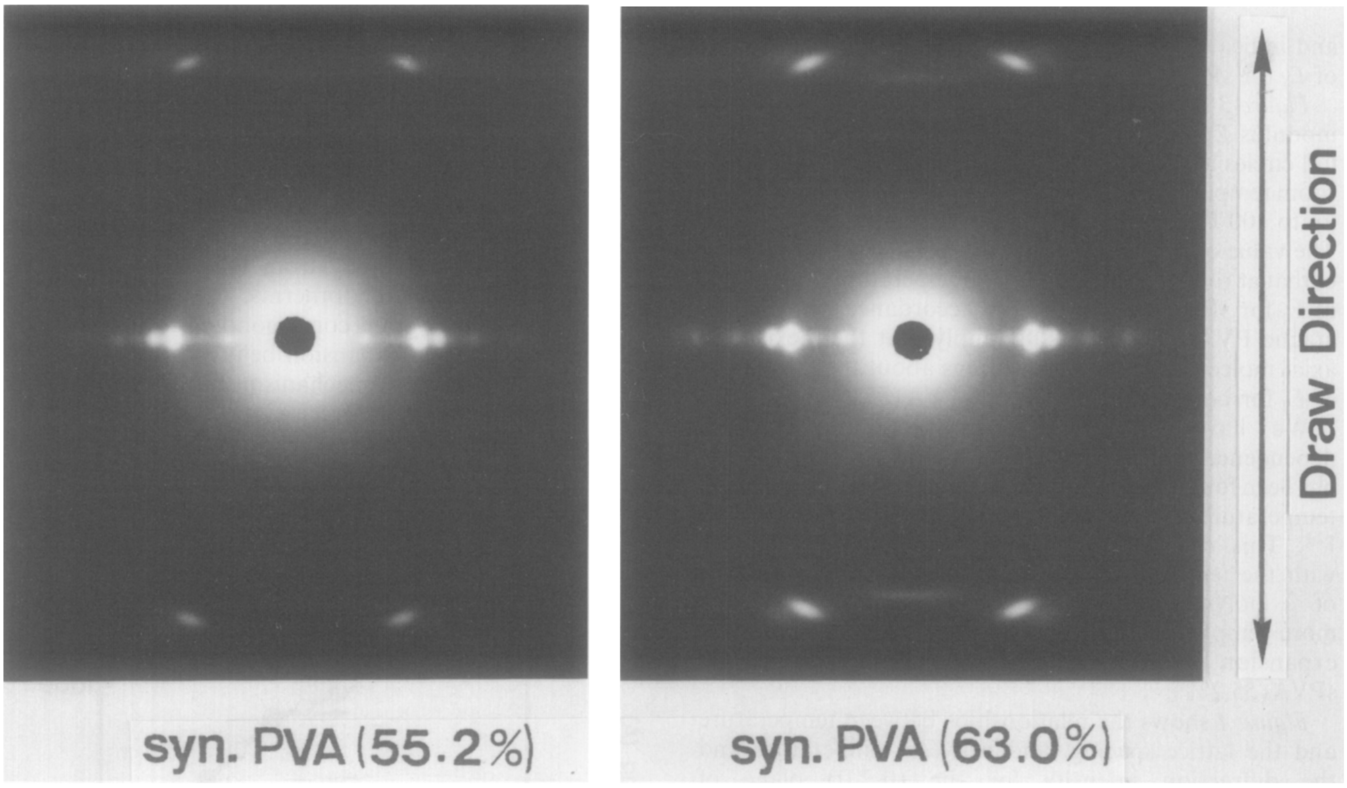

Figure 1 X-ray fibre photographs of syndiotactic poly(vinyl alcohol)

Table 2 Characteristics of various poly(vinyl alcohols) with different tacticities

	aPVS	sPVA(55.2%)	sPVA(63.0%)
Syndiotacticity from i.r. (%)	45.0	55.2	63.0
Specimen modulus (GPa)	12.3	27.8	17.5
Crystallite size (0 2 0) (Å)	128	104	86
Density (g cm^{-3})	1.310	1.312	1.309
Crystallinity (%)	55.0	57.7	54.6
Melting point (°C)	250	242	254
Heat of fusion (cal g^{-1})	18.8	21.1	23.6
Degree of orientation	0.969	0.977	0.964

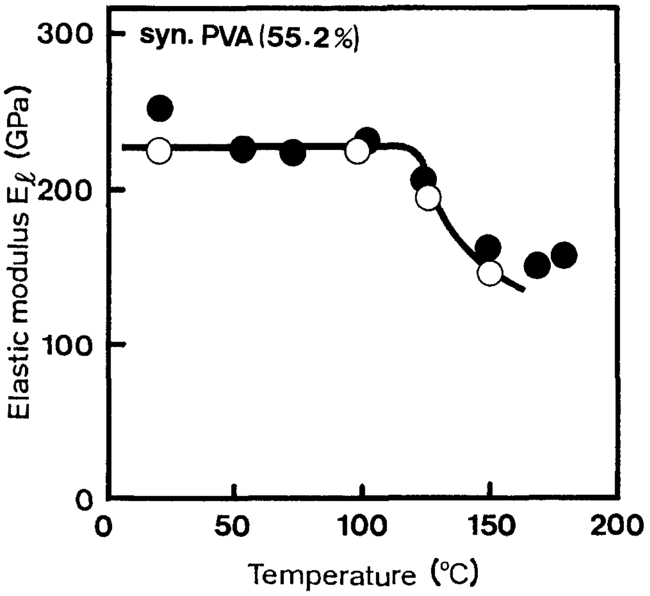

Figure 3 Effect of temperature on the elastic modulus E_l for the (0 2 0) plane of sPVA(55.2%) (○). Also shown are results for atactic poly(vinyl alcohol) (●)

and indicate that there exists a temperature dependence of E_l for sPVA(55.2%).

Figure 3 shows the effect of temperature on the elastic modulus E_l for the (0 2 0) plane of sPVA(55.2%). The full circles also indicate the results for atactic PVA[10]. At room temperature, E_l was 235 GPa. It remained constant up to 100°C, followed by a rapid decrease above 120°C. The value of E_l was 146 GPa at 150°C, which is ca. 62% of that at room temperature. The temperature dependence of E_l for sPVA(55.2%) was in accordance with that of atactic PVA[10]. These results imply that there exists an axial molecular motion that brings about the decrement of E_l for both atactic PVA and sPVA(55.2%).

We have already investigated the temperature dependence of E_l for various polymers[5,10–12,20–23]. It has been found that the E_l value decreased above a certain temperature, except for PET[20], P4M1P[23] and cellulose I[21]. This characteristic temperature is in accordance with the temperature range where thermal contraction of a polymer chain in the crystalline regions was more emphasized. Thus, we measured the thermal expansion behaviour of the crystal lattice for sPVA(55.2%).

Figure 4 shows the relationships between temperature and the lattice spacing, and between temperature and the diffraction intensity for the (0 2 0) plane of sPVA(55.2%). Measurements were performed during both a heating (open circles) and a cooling (full circles) process, and were found to be reversible. With increasing temperature, the lattice spacing for the (0 2 0) plane, which is a half of the fibre identity period, decreased with an inflection point around 120°C. The thermal expansion coefficient α_c changed from $-3.5 \times 10^{-6}\,K^{-1}$ to $-9.0 \times 10^{-6}\,K^{-1}$ across 120°C. The diffraction intensity also decreased at high temperature, with an inflection point around 120°C. In general, the diffraction intensity decreases with increasing temperature owing to the thermal vibration of atoms as indicated by the Debye–Waller factor[24]. Accordingly, the decrement of the intensity is considered to be due to the increment of the incoherent thermal vibration of the chain molecules in the crystalline regions. In particular, some large-amplitude vibration is considered to be more enhanced above 120°C. Comparing the temperature dependence of E_l with those of the lattice spacing and the diffraction intensity for the (0 2 0) plane of sPVA(55.2%), they resenble one another. The same phenomenon was also observed for atactic PVA[10]. Thus, the abrupt change in the mobility of chain molecules in the crystalline regions is considered to cause the decrement of E_l above 120°C.

Molecular motions of the chain molecules in the crystalline regions of PVA have been pointed out by numerous kinds of measurements. Nagai observed the abrupt change in relative infra-red absorption ratio of the crystalline band (8.7 μm) and non-crystalline band (9.1 μm) at 120°C, and reported that torsional molecular motion of the chain in the crystalline regions was activated above 120°C[25]. Yano reported an inflection point around 120°C in specific volume–temperature measurements[26]. Nagai *et al.* detected two adsorptions due to the motion in the crystalline regions, the first at 120°C and the second in the vicinity of 200°C, by dynamic viscoelasticity measurements[27]. They assigned the former as β_c dispersion corresponding to an increment in the amplitude of rotational motion of the chain due to weakening of intermolecular interaction accompanied by lattice thermal expansion. Further, Shirakashi *et al.* reported the thermal expansion behaviour of the crystal lattice of atactic PVA[28]. They found that the thermal expansion coefficients for the (2 0 0), (0 0 1) and (0 2 0) planes changed discontinuously around 120°C, and attributed these to a second-order transition of the crystal. They also reported that this transition was not due to translational motion but to highly restricted rotational motion, judging from the anisotropy of α_c. Kenney observed the endothermic peak around 120°C in the d.t.a. thermogram corresponding to an inflection point of the thermal expansion behaviour of the crystal lattice[29]. Though many mechanisms have been reported, as shown above, the precise molecular origin has remained obscure till now. At any rate, the decrement of E_l indicates that molecular motion in a direction parallel to the chain axis is enhanced at high temperature. At this

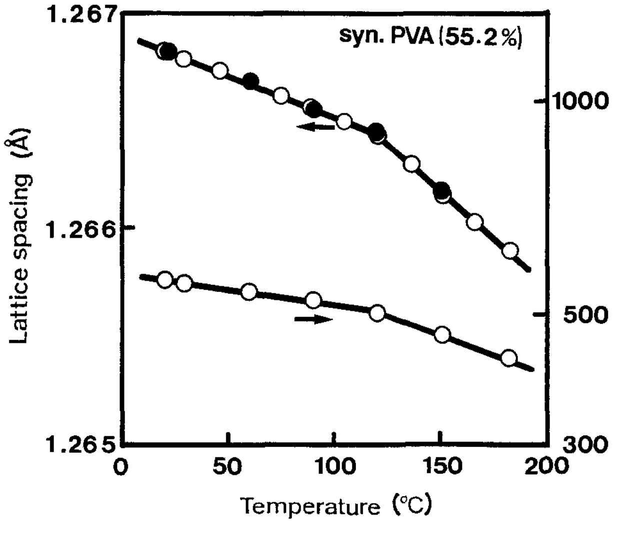

Figure 4 Effect of temperature on the lattice spacing and the diffraction intensity for the (0 2 0) plane of sPVA(55.2%): both the heating (○) and the cooling (●) processes are shown

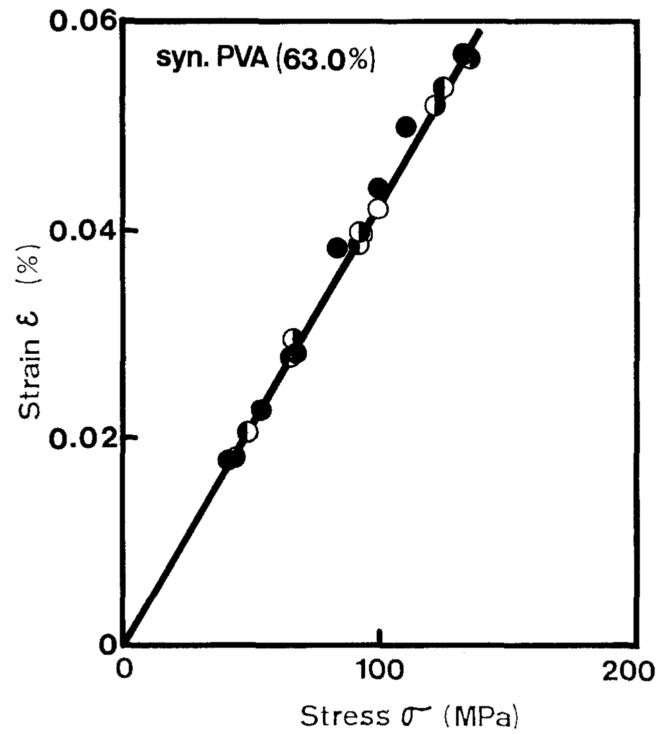

Figure 5 Stress–strain curves for the (0 2 0) plane of sPVA(63.0%) at various temperatures: (○) 18°C, (◐) 100°C, (◑) 125°C, (●) 150°C

point, we adopt the kinked-chain model, where two *gauche* conformations are incorporated in the otherwise all-*trans* chain as the sequence $\cdots TTTTGT\bar{G}TTTT\cdots$ (ref. 30), and we succeeded in reproducing the decrement of E_l for atactic PVA at high temperature quite well[11]. Thus, also in the case of sPVA(55.2%), a mechanism of axial chain deformation becomes involved in the internal rotation through the incorporation of a small amount of a very contracted portion such as a kink at high temperature.

Nagura *et al.* investigated the wavenumber of the infra-red absorption assigned to the OH stretching in the crystalline regions of partially deuterated PVA as a function of temperature[31]. They found that the wavenumber shifted to high frequency with temperature owing to the weakening of hydrogen bonds, and this tendency is more enhanced above 120°C for atactic PVA and sPVA(54%). On the other hand, the wavenumber shifted only monotonically with temperature for sPVA(65%). They also reported that the intensity of mechanical tan δ decreased with increasing syndiotacticity and crystallinity of PVA[32]. These results were explained by the dense packing of chains in the crystal lattice and the tight intermolecular hydrogen bonds for highly syndiotactic PVA. In addition, there were many reports that the properties of PVA changed drastically with its tacticity[13,14]. We investigated the temperature dependence of E_l of highly syndiotactic (63.0%) PVA.

Figure 5 shows the stress–strain (σ–ε) curves for the (0 2 0) plane of sPVA(63.0%) at various temperatures. All the plots at different temperatures coincided with one another for sPVA(63.0%). Again, the lattice extensions were always reversible.

Figure 6 shows the effect of temperature on the elastic modulus E_l of sPVA(63.0%) calculated from the slope of the σ–ε curves in *Figure 5*. The value of E_l remained constant till 150°C, in contrast with the results for sPVA(55.2%) (*Figure 3*). Tashiro *et al.* calculated the E_l values for sPVA with and without taking into consideration the intermolecular interaction[33]. They reported that the calculated value was affected only negligibly by intermolecular interaction (with, 287.4 GPa; without, 287.2 GPa). Thus, the difference in the temperature dependence of E_l for various PVAs is not considered to be due to the stiffening effect of intermolecular hydrogen bonds. On the contrary, when the tacticity changes from syndiotactic to isotactic, the direction of hydrogen bonding changes from perpendicular to parallel to the chain axis for PVA[34]. In this case, the calculated E_l value was reported to increase for isotactic PVA (323 GPa)[35]. This means that the intramolecular hydrogen bonds, in other words, the increment of isotactic sequence, introduce some stiffness into the PVA chain. However, these phenomena were not observed for PVA at room temperature within the difference of tacticity level studied. To conform this point, further experiments on extremely highly syndiotactic and isotactic PVA will be needed. Investigations on the E_l value at low temperature are now continued.

As shown above, the decrement of E_l for sPVA(55.2%) coincided with the change in axial thermal contractivity. On the other hand, when the thermal expansion coefficient was constant, such as for PET[20], P4M1P[23] and cellulose I[21], the E_l value was found to remain constant even at high temperature.

Figure 7 shows the relationships between temperature and the lattice spacing, and between temperature and the diffraction intensity for the (0 2 0) plane of sPVA (63.0%). Again, the heating and cooling process was reversible. With increasing temperature, both the lattice spacing and the diffraction intensity for the (0 2 0) plane decreased monotonically without having an inflection point, in contrast with those of sPVA(55.2%) (*Figure 4*). The thermal expansion coefficient was $-3.3 \times 10^{-6}\,\mathrm{K}^{-1}$, which coincides with that of sPVA(55.2%) in the low-temperature region. This indicates that the molecular motion that brings about the decrement of E_l that was observed for sPVA(55.2%) does not occur for sPVA(63.0%). This may be due to the strong

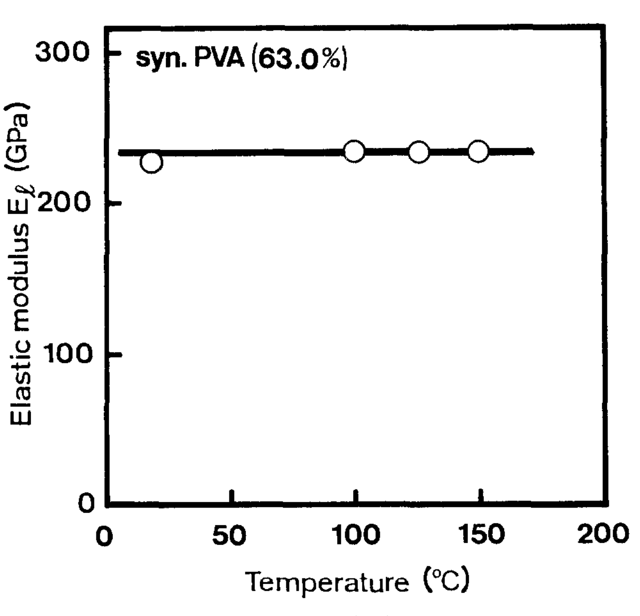

Figure 6 Effect of temperature on the elastic modulus E_l for the (0 2 0) plane of sPVA(63.0%)

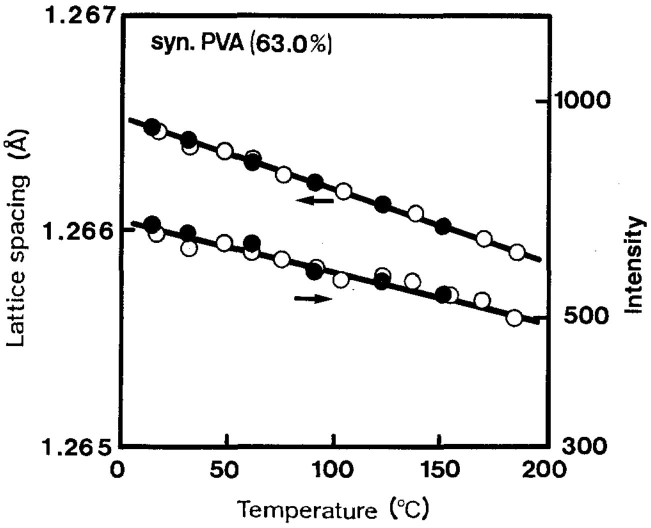

Figure 7 Effect of temperature on the lattice spacing and the diffraction intensity for the (0 2 0) plane of sPVA(63.0%): both the heating (○) and the cooling (●) processes are shown

intermolecular hydrogen bonds for highly syndiotactic PVA, because the strong interactions are expected to restrict the molecular motion in the crystal lattice. Accordingly, the decrement of E_l at high temperature is due to the incorporation of a small amount of a contracted portion, such as kinks, into the chain, and this kind of molecular motion is considered not to occur for sPVA(63.0%). Further, these results indicate that increasing the syndiotacticity is one of the most effective ways to confer high heat resistance to PVA.

REFERENCES

1 Sakurada, I., Nukushina, Y. and Ito, T. *J. Polym. Sci.* 1962, **57**, 65
2 Sakurada, I., Ito, T. and Nakamae, K. *J. Polym. Sci.* (*C*) 1966, **15**, 75
3 Sakurada, I. and Kaji, K. *J. Polym. Sci.* (*C*) 1970, **31**, 57
4 Nakamae, K., Nishino, T., Shimizu, Y. and Matsumoto, T. *Polym. J.* 1987, **19**, 451
5 Nakamae, K. and Nishino, T. Proc. 5th Rolduc Conf., Elsevier Applied Science, London, 1990
6 Lemstra, P. J., Kirschbaum, R., Ohta, T. and Yasuda, H. 'Developments in Oriented Polymers-2' (Ed. I. M. Ward), Elsevier Applied Science, London, 1987, Ch. 2
7 Kunugi, T. and Kawasumi, T. 32nd Int. Symp. on Macromolecules, Preprint, 1988, p. 431
8 Nakamae, K., Nishino, T. and Kageoka, M., Kobe Annual Meeting of Polymer Science, Preprint, 1990, Vol. 36, p. 94
9 Yamaura, K., Tanigami, T., Hayashi, N., Kosuda, K., Okuda, S., Takemura, Y., Itoh, M. and Matsuzawa, S. *J. Appl. Polym. Sci.* 1990, **40**, 905
10 Nakamae, K., Nishino, T., Hata, K. and Matsumoto, T. *Kobunshi Ronbunshu* 1986, **43**, 133
11 Nishino, T., Ohkubo, H. and Nakamae, K. *J. Macromol. Sci–Phys.* (*B*) to be published
12 Nakamae, K., Nishino, T., Shimizu, Y. and Hata, K. *Polymer* 1990, **31**, 1909
13 Matsuzawa, S. and Ueberreiter, K. *Colloid Polym. Sci.* 1978, **256**, 490
14 Yamaura, K. and Matsuzawa, S. *Kobunshi Kako* 1972, **21**, 248
15 Matsuzawa, S., Yamaura, K., Noguchi, H. and Hayashi, H. *Makromol. Chem.* 1973, **165**, 217
16 Murahashi, S., Nozakura, S., Sumi, M., Yuki, H. and Hatada, K. *Kobunshi Kagaku* 1966, **23**, 605
17 Sakurada, I., Fuchino, K. and Okada, A. *Kaken Hokoku* 1950, **23**, 78
18 Sakurada, I., Nukushina, Y. and Sone, Y. *Kobunshi Kagaku* 1955, **12**, 506
19 Nakamae, K., Nishino, T. and Ohkubo, H. *J. Macromol. Sci.–Phys.* (*B*) 1991, **30**, 1
20 Nakamae, K., Nishino, T., Tokoyama, F. and Matsumoto, T. *J. Macromol. Sci.–Phys.* (*B*) 1988, **27**, 407
21 Nishino, T., Takano, K. and Nakamae, K. *Polym. Prepr. Jpn* 1990, **39**, 1176
22 Nakamae, K., Nishino, T., Shimizu, Y., Hata, K. and Matsumoto, T. *Kobunshi Ronbunshu* 1986, **43**, 499
23 Nakamae, K., Nishino, T. and Takagi, S. *J. Macromol. Sci.–Phys.* (*B*) 1991, **30**, 47
24 Tadokoro, H., 'Structure of Crystalline Polymers', Wiley Interscience, New York, 1976, p. 62
25 Nagai, E. 'Polyvinyl Alcohol' (Ed. I. Sakurada), The Society of Polymer Science, Japan, 1956, p. 245
26 Yano, Y. *Busseiron Kenkyu* 1956, **94**, 163
27 Nagai, A. and Takayanagi, M. *Rep. Prog. Polym. Phys. Jpn.* 1964, **8**, 249
28 Shirakashi, K., Ishikawa, K. and Miyasaka, K. *Kobunshi Kagaku* 1964, **21**, 234
29 Kenney, J. F. and Willcockson, G. W. *J. Polym. Sci.* (*A*) 1966, **1**, 679
30 Pechhold, W. *Kolloid-Z.* 1963, **189**, 14; 1968, **228**, 1; 1970, **241**, 955
Reneker, D. H. and Mazur, J. *Polymer* 1984, **25**, 1549
31 Nagura, M., Matsuzawa, S., Yamaura, K. and Ishikawa, H. *Polym. J.* 1982, **14**, 69
32 Nagura, M., Matsuzawa, S., Yamaura, K. and Ishikawa, H. *Polym. Commun.* 1983, **24**, 250
33 Tashiro, K., Kobayashi, M. and Tadokoro, H. *Macromolecules* 1977, **10**, 731
34 Murahashi, S., Yuki, H., Sano, T., Yonemura, U., Tadokoro, H. and Chatani, Y. *J. Polym. Sci.* 1962, **62**, S77
35 Tashiro, K. *Kaigai Kobunshi Kennkyu* 1986, **32**, 196