

SHORT COMMUNICATION

Tacticity Dependence of Molecular Motion in Crystal of Poly(vinyl alcohol)

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Molecular motion in atactic poly(vinyl alcohol) (PVA) was studied first by Yano.¹ Two second order transition points were found at 80°C and 120°C by dilatometry, but Yano was unable to explain what type of molecular motion occurred at the higher transition point. Shirakashi *et al.*² observed a transition at 120°C in the measurement of temperature dependence of the lattice spacings of d_{100} and d_{001} for atactic PVA, and considered that a restricted molecular motion, different from the thermal vibration in the crystal lattice, occurred above 120°C.

It is expected that the increase in the syndiotacticity of the PVA samples causes a dense molecular packing in the crystal and also stronger intermolecular hydrogen bonds are responsible for the disappearance of the molecular motion. In this paper, we investigated by X-ray and infrared methods how the molecular motion and the strength of the intermolecular hydrogen bonds depend on the syndiotacticity.

EXPERIMENTAL

Three PVA samples were used: a) atactic PVA fibers made by saponification of poly(vinyl acetate) (PVA_{fiber}), b) PVA film bulk-polymerized from vinyl trifluoroacetate and saponified (PVA_{s54}), c) PVA film solution-polymerized from vinyl trifluoroacetate and saponified (PVA_{s65}).³

Table I gives the characterization of the samples, where the degree of polymerization was estimated by viscometry, the syndiotacticity by Murahashi's

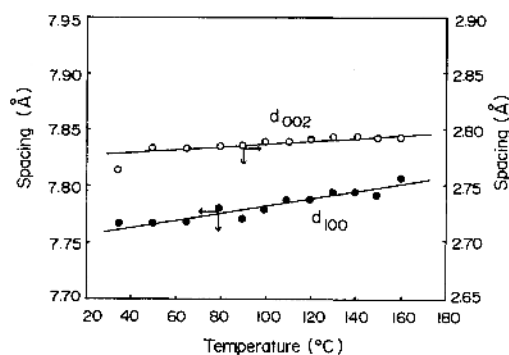
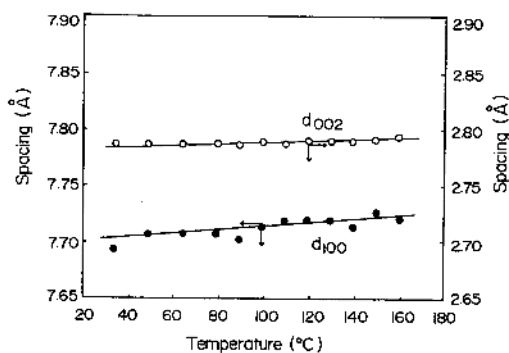
procedure^{4,5,6} utilizing the optical density ratios of the infrared absorption bands at 916 and 849 cm⁻¹, the concentration of the head-to-head linkage by Ito's process,⁷ and the degree of crystallinity by Herman's method from the X-ray diffraction curve. The films of the highly syndiotactic PVA_{s54} and PVA_{s65} were prepared in the following way: a 5% aqueous solution, prepared in a glass tube by dissolving the polymer at 130°C for 30 min, was dried on a hot glass plate held at 90°C. After drying *in vacuo* at 100°C for 2 h, the cast film was drawn to three times its original length and annealed at 200°C for 2 min in a silicone oil bath. X-ray diffraction was measured by a Rigaku Geigerflex 2028 diffractometer equipped with a scintillation counter and a pulse height analyser using the CuK α radiation. The temperature was controlled within an accuracy of $\pm 0.5^\circ\text{C}$ under N₂ gas flow. Infrared measurement was made by a JASCO A-302 infrared spectrophotometer equipped with a heating device. The infrared spectra were measured on KBr tablets for PVA_{fiber} and films for PVA_{s54} and PVA_{s65} sandwiched between two NaCl plates. The OH groups in the amorphous part were deuterated according Tadokoro's method⁸ after drying the samples *in vacuo* for 4 h at 110°C.

RESULTS AND DISCUSSION

Figures 1 and 2 show the temperature dependence of the (100) and (002) spacings for PVA_{s54} and PVA_{s54} and PVA_{s65}, respectively. The spacings increase linearly with temperature without any abrupt

Table I. The characterized values for three kinds of PVA samples

	Degree of polymerization	Syndio-diad tacticity	Head-to-head linkage	Degree of crystallinity
		%	mol%	%
PVA _{fiber}	1700	34	2	38
PVA _{s54}	2100	54	1	48
PVA _{s65}	3315	65	0.5	61

**Figure 1.** Temperature dependence of the spacings of 100 and 002 reflections for PVA_{s54}.**Figure 2.** Temperature dependence of the spacings of 100 and 002 reflections for PVA_{s65}.**Table II.** The linear thermal expansion coefficients and spacings for three kinds of PVA samples

Sample	Linear thermal expansion coefficient, α		Spacing	
	$^{\circ}\text{C}^{-1}$		Å	
	α_{100}	α_{001}	d_{100}	d_{001}
PVA _{fiber}	9.3×10^{-5a} 10×10^{-5b}	5.3×10^{-5a} 4×10^{-5b}	7.81 ~ 7.83	5.51 ~ 5.53
PVA _{s54}	4.0×10^{-5}	4.7×10^{-5}	7.76	5.56
PVA _{s65}	2.0×10^{-5}	2.7×10^{-5}	7.71	5.56

^a Ref 9.^b Ref 2.

change in the slope, indicating an ordinary thermal expansion of the lattice. This is different from the case of atactic PVA_{fiber} where incoherent thermal molecular motion was shown by Shirakashi *et al.*² The linear thermal expansion coefficient (α) were

calculated from the slopes of the lines in Figures 1 and 2. The values are given in Table II along with the results for atactic PVA reported by Shirakashi *et al.*² and Nitta *et al.*⁹ The thermal expansion was found to be isotropic for highly syndiotactic PVA_{s54}

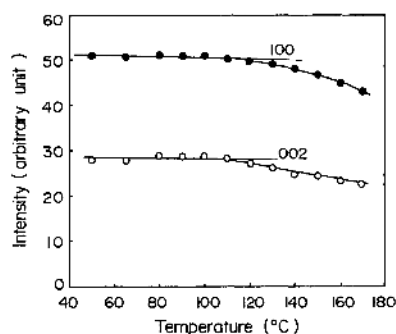


Figure 3. Temperature dependence of the X-ray diffraction intensities of 100 and 002 reflections for PVA_{s54}.

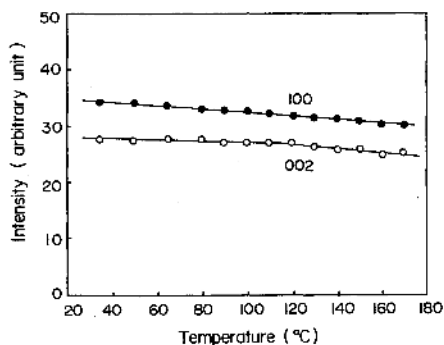


Figure 4. Temperature dependence of the X-ray diffraction intensities of 100 and 002 reflections for PVA_{s65}.

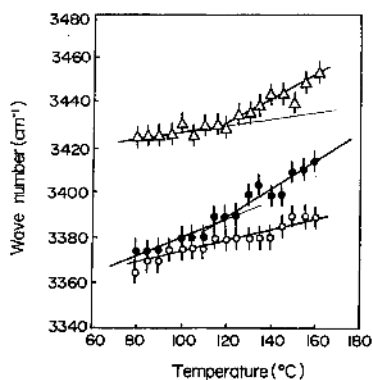


Figure 5. Temperature dependence of the wave number of the absorption band of -OH stretching for PVA_{fiber} (Δ), PVA_{s54} (\bullet), and PVA_{s65} (\circ).

and PVA_{s65}, in contrast to the case of atactic PVA. This isotropic expansion may be related to the decrease in d_{100} by about 1.5%, and the increase in d_{001} by about 0.5%, compared to the atactic PVA.

Figures 3 and 4 show the temperature dependence of the X-ray diffraction intensities of the (100) and (002) reflections for PVA_{s54} and PVA_{s65}, respectively. The intensities decrease monotonously with temperature. For PVA_{s54}, the slope changes abruptly at 120°C, suggesting the occurrence of some large-amplitude molecular motion. This transition could not be detected in Figure 1, since the sensitivity in the spacing measurement was insufficient. On the other hand, the highest syndiotactic PVA_{s65} sample exhibited no such transition.

Figure 5 shows the wave number of the maximum infrared absorption due to the OH stretching in the crystalline region of PVA_{fiber}, PVA_{s54}, and PVA_{s65} as a function of temperature. These samples were deuterated by 61%, 53%, and 42%, respectively, the degree of deuteration being estimated by the ratio of the integrated intensity of the OD stretching band to the sum of the intensities of the OD and the OH stretching bands. These values are almost consistent with the fraction of the amorphous region estimated from the degree of crystallinity. Thus, the undeuterated OH groups are in the crystalline region.* Hence the wave number shifts seen in Figure 5 may possibly be due to a structural change occurring in the crystalline region of these samples. The slope of the line in Figure 5 changes abruptly at 120°C for PVA_{fiber} and PVA_{s54}, but does not for PVA_{s65}. The high frequency shift of the maximum absorption band with increasing temperature indicates that the intermolecular hydrogen bonds are weakened by some thermal motion. These results thus suggest that only the thermal molecular vibration in the crystal lattice occurs in the highest syndiotactic PVA_{s65}, while the incoherent molecular motion occurs above 120°C for PVA_{fiber} and PVA_{s54}. The reason as to why this incoherent molecular motion occurs in the crystal of PVA_{fiber} and PVA_{s54} can be explained as follows. The OH stretching band appears at a higher wave number for these samples than for PVA_{s65} in the measured temperature range. Thus, with decreasing syndiotacticity, the number of intermolecular hydrogen bonds decreases. On the other hand, the concentration of head-to-head linkages is higher for PVA_{fiber} and PVA_{s54} than for

* According to Tadokoro *et al.*,⁸ the PVA molecules in the crystalline region were also deuterated by repeated deuteration, while in this work they were not deuterated. This disagreement is due to the only one cycle of deuteration in this work.

PVA_{s65} (Table I), implying that there are more $\{-\text{CH}_2\}_2$ groups in the former two samples than in the last one. The weaker intermolecular hydrogen bonds and the existence of more $\{-\text{CH}_2\}_2$ groups increases the mobility of the molecular chain, followed by incoherent molecular motion above 120°C.

Strong intermolecular hydrogen bonds in the highly syndiotactic PVA_{s65} sample may cause the isotropic thermal expansion with a comparatively small thermal expansion coefficient.

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