

Structure and Properties of Syndiotacticity-Rich Poly(vinyl alcohol) Prepared Through Saponification of Drawn Poly(vinyl trifluoroacetate) with Gaseous Ammonia

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ABSTRACT: The structure and properties of syndiotacticity-rich poly(vinyl alcohol) (s-PVA) prepared through the saponification of drawn poly(vinyl trifluoroacetate) (PVTFAc) with gaseous ammonia were studied. The PVTFAc samples with s-diad % of 59 and 64 were used. The s-PVAs had low densities and showed X-ray diagrams similar to the fiber diagram of PVA with indistinct 100, 101, 10 $\bar{1}$, and 200 plane reflections and without the plane reflections seen at the equator of a typical fiber diagram, such as 001, 201, and 002. The s-PVAs had melting points comparable to those of saponified and heat-drawn samples, indicating a PVA with the typical fiber structure as seen in the X-ray diagram of a sample. The intensity of the 916 cm⁻¹ band in the infrared spectrum related to syndiotactic diads decreased with drawing, suggesting an increase in the crystallinity. Crystals with more defects are thought to be produced in saponification. The s-PVA films drawn 16 times and saponified had a Young's modulus and strength at break of 22 and 1.5 GPa for the sample from S-59 and 14 and 1.2 GPa for the sample from S-64, respectively. The crystallization-sensitive band of 1145 cm⁻¹ in the infrared spectra of the saponified samples was weak. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 80: 467–474, 2001

Key words: poly(vinyl trifluoroacetate); drawing; saponification; poly(vinyl alcohol); crystals with defects; high modulus; high strength

INTRODUCTION

Syndiotacticity-rich poly(vinyl alcohol) (s-PVA) has greater hot-water resistance¹ and heat resistance² than those of atactic PVA (commercial PVA). Films with the practical mechanical properties of heat-drawn solid s-PVA can be prepared from aqueous solutions by casting at higher tem-

peratures² since aqueous solutions gel easily at room temperature.³ The aqueous solutions of s-PVA are prepared by dissolving it in water above 100°C in sealed vessels. Therefore, the preparation of s-PVA films is not easy. Poly(vinyl trifluoroacetate) (PVTFAc) has been known to be saponified in the solid state with gaseous ammonia.^{4,5} The saponification is considered to be promising for the preparation of PVA film since PVTFAc films can be prepared easily from its acetone solutions. The molecules were clarified to be arranged laterally but not to form crystals when stretched PVTFAc is saponified in the solid state. No detailed investigation on the structure and properties of the s-PVA prepared by saponi-

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Table I Preparation of PVTFac

Sample No.	Polymerization Conditions			Triad (%) ^b			
	Initiator	Temperature (°C)	DP ^a	<i>I</i>	<i>H</i>	<i>S</i>	s-Diad %
S-59	BPO (0.05%)	60	2130	16.2	49.6	34.2	59.0
S-64	Benzophenone (0.05%) -THF (4.8 vol %) (photosensitizer)	-78	1080	13.8	44.4	41.8	64.0

^a Determined by viscometry for saponified and acetylated sample.⁶

^b Determined by NMR for saponified sample in DMSO-*d*₆ (Bruker DRX-500).⁷

fication has been carried out. We report on the investigation of the samples drawn to different ratios and saponified, using density measurement, X-ray and thermal analyses, infrared spectra, and mechanical properties.

EXPERIMENTAL

Samples

Two kinds of PVTFac with different syndiotacticities (S-59 and S-64), as shown in Table I, were used. The degrees of polymerization (DP) were determined by viscometry for the s-PVA prepared by solid-state saponification with gaseous ammonia after acetylation, using the equation $[\eta]$

$= 8.91 \times 10^{-3} \text{DP}^{0.62}$ (benzene).⁶ The contents of isotactic (*I*), heterotactic (*H*), and syndiotactic (*S*) triads were estimated for s-PVA from ¹³C-NMR measurements in dimethyl sulfoxide *d*₆ solutions using a Bruker DRX-500 NMR spectrometer.⁷ The s-diad % was estimated as $\text{s-diad \%} = S + (1/2)H$, assuming simple Markovian propagation in polymerization. PVTFac changes slowly, releasing trifluoroacetic acid during storage. Thermally polymerized PVTFac was used within 1 year, and photoinduced polymerized PVTFac, within 3 months.

Preparation of Films

The films were prepared by casting acetone solutions.

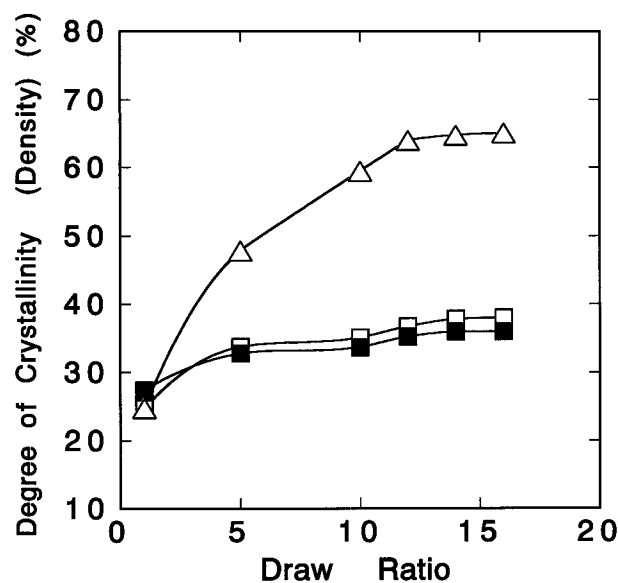


Figure 1 Dependencies of degree of crystallization estimated from density of drawn and saponified (D-S), and saponified and drawn (S-D) PVTFac on draw ratio: (□) S-59 (D-S); (■) S-64 (D-S); (△) S-59 (S-D).

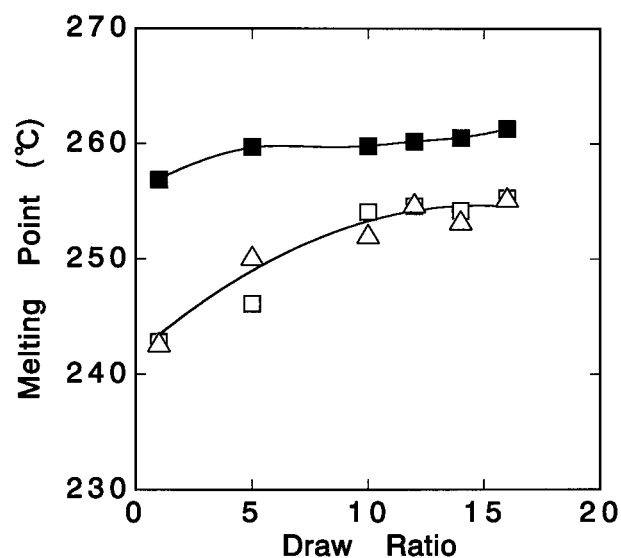


Figure 2 Dependencies of melting point of drawn and saponified (D-S) and saponified and drawn (S-D) PVTFac on draw ratio: (□) S-59 (D-S); (■) S-64 (D-S); (△) S-59 (S-D).

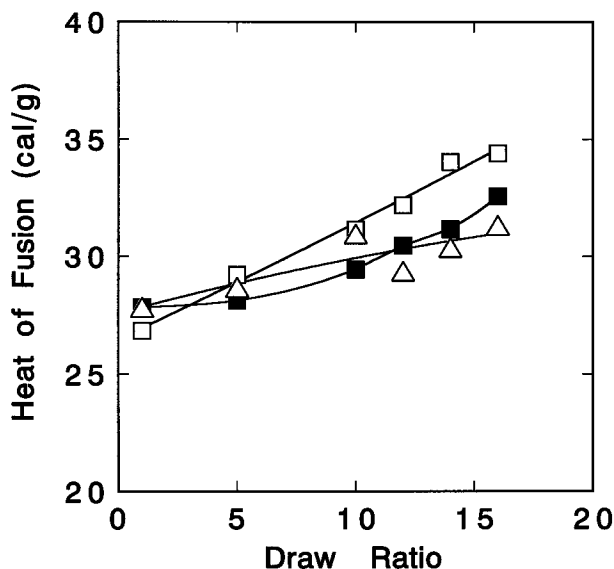


Figure 3 Dependencies of heat of fusion of drawn and saponified (D-S), and saponified and drawn (S-D) PVTFAc on draw ratio: (□) S-59 (D-S); (■) S-64 (D-S); (△) S-59 (S-D).

Drawing

PVTFAc films were drawn at 140°C (partly at 100°C) in an oven with a drawing apparatus. The undrawn/saponified s-PVA was drawn at 210°C.

Saponification

Drawn and undrawn films were saponified in a box with dry gaseous ammonia for 3 h at room temperature, followed by washing with methanol and drying at room temperature in a vacuum.

Density

The density of s-PVA was determined by a flotation method using a benzene-carbon tetrachloride system. Degrees of crystallization (X) were estimated from the density using the equation $1/d = (1 - X)/1.269 + X/1.345$ (ref. 8), where d is the density of the sample.

X-ray Analyses

X-ray diagrams were obtained with Ni-filtered $\text{CuK}\alpha$ X-rays from a Shimadzu XD-610 X-ray generator at 30 kV and 30 mA.

Infrared Spectra

The infrared spectra were obtained with a Nippon Bunko FTIR spectrometer.

Thermal Properties

The melting point and heat of fusion (ΔH) were determined by differential scanning calorimetry using a MAC Science DSC 3200.

Mechanical Properties

The Young's modulus and strength at break were measured with a Minebea TCM-50J-L tensile tester. The data are the mean of the values of five samples.

RESULTS AND DISCUSSION

Figure 1 shows the degree of crystallization estimated from the density and draw ratio for drawn/saponified and saponified/drawn samples. Each drawn/saponified sample has a lower density and appears to have a lower degree of crystallization than those of the saponified/drawn sample at each

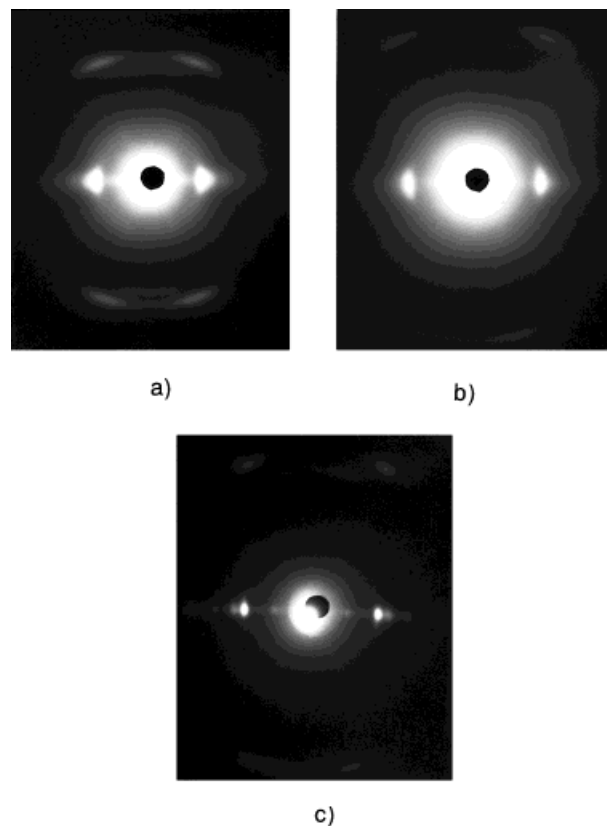


Figure 4 X-ray diagrams of (a) drawn (13 × at 100°C)/saponified (S-54, camera distance: 40 mm), (b) drawn (13 × at 140°C)/saponified (S-64, camera distance: 50 mm), and (c) saponified/drawn (13 × at 100°C) (S-54, camera distance: 50 mm).

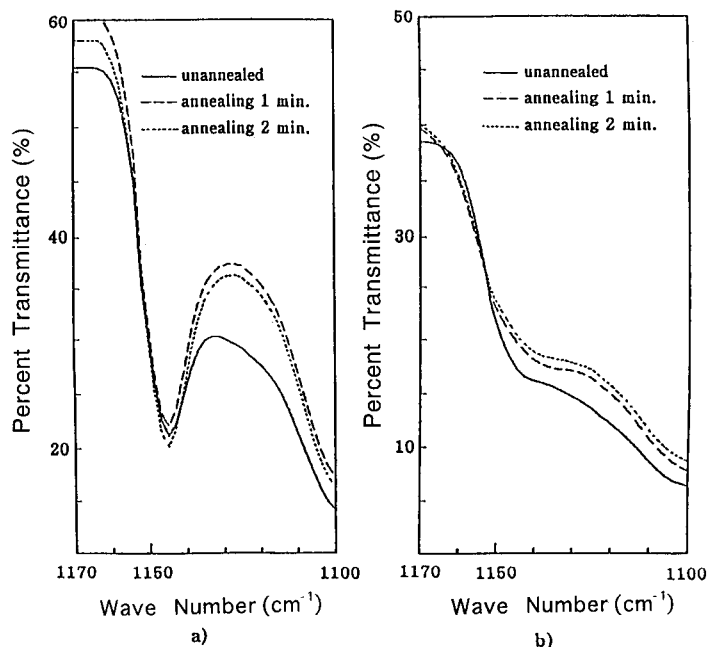


Figure 5 Change of intensities of crystallization-sensitive bands of PVA films with heating (200°C) time: (a) from as-cast PVTFAc (S-59) film; (b) from drawn ($4 \times$ at 100°C) PVTFAc (S-59) film.

fixed draw ratio. Figures 2 and 3 show the relationships between the melting point or heat of fusion and draw ratio. In drawn/saponified samples, the s-PVA derived from S-64 has a higher

melting point than that of the s-PVA derived from S-59 at a fixed draw ratio. This suggests that the former has more stable crystals with more intermolecular hydrogen bonds than in the latter. In

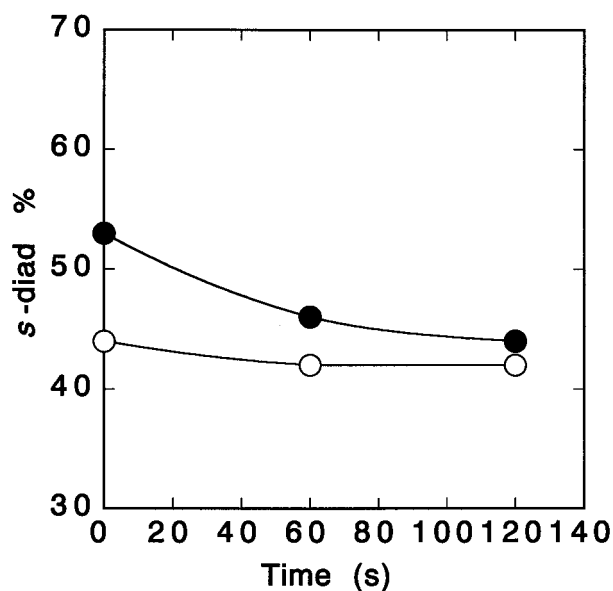


Figure 6 Dependencies of s-diad % content of solid-state saponified PVTFAc (S-59) on heating (200°C) time. (●) undrawn; (○) drawn ($4 \times$ at 100°C).

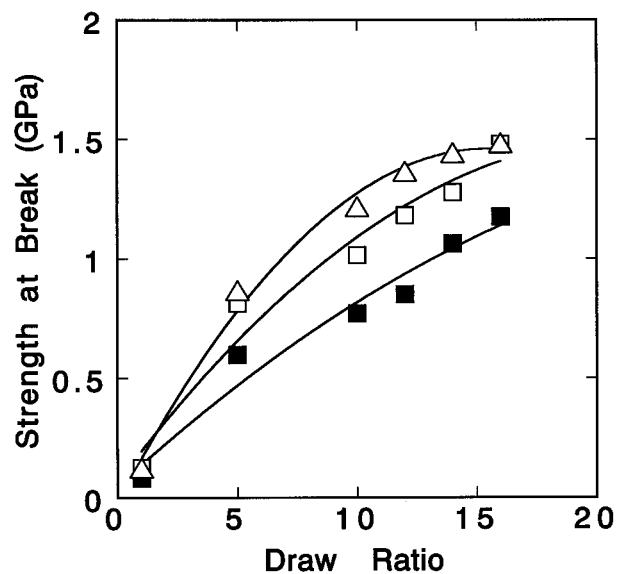


Figure 7 Dependencies of strength at break of drawn and saponified (D-S) and saponified and drawn (S-D) PVTFAc on draw ratio: (□) S-59 (D-S); (■) S-64 (D-S); (△) S-59 (S-D).

the s-PVA derived from S-59, the drawn/saponified sample has a melting point similar to that of the saponified/drawn sample at a fixed draw ratio, meaning that both samples have crystallites of the same size and structure or different structures with the same ratio of the enthalpy of fusion to the entropy of fusion. The heat of fusion of the drawn/saponified samples derived from S-59 is higher than that of saponified/drawn samples at a fixed draw ratio. If 49 cal/g is assumed as the heat of fusion for the complete crystals⁹ and both samples have crystallites of the same size, the degree of crystallization for the drawn/saponified sample with the draw ratio of 15 is 69% ($34/49 \times 100$) and that for the saponified/drawn sample with the same draw ratio is 65% ($32/49 \times 100$), which agrees with that estimated from the density. If the heat of fusion of the complete crystals for the saponified/drawn sample is low, the degree of crystallization based on the crystals is higher than 69%. For drawn/saponified samples, the melting point is higher and the heat of fusion is lower for those derived from S-64 than for those derived from S-59 at a fixed draw ratio. If the degree of crystallization is the same for both samples, the entropy of fusion of the former is lower than that of the latter. In the case of S-59, if the degree of crystallization of a saponified/drawn sample is higher than that of the drawn/saponified sample, as discussed above, the entropy of fusion of the former is estimated to be lower than that of the latter. The melting point and heat of fusion increase gradually with increasing draw ratio. This is due to the increase in the degree of crystallization.

Figure 4 shows X-ray diagrams of the drawn/saponified samples [Fig. 4(a,b)] and the saponified/drawn samples [Fig. 4(c)]. Although Figure 4(a,b) is similar to the fiber diagram of PVA, the indistinct reflections due to 100, 101, $10\bar{1}$, and 200 planes are observed and the reflections due to planes such as 001, 201, and 002 are not at the equator, unlike those reported previously.⁴ In Figure 4(b), the diagram of the sample derived from S-64 is more diffuse than is that derived from S-59. Figure 4(c) is the typical fiber diagram known for heat-stretched solid PVA. In the crystals of the drawn/saponified samples, PVA molecules are arranged parallel to the stretched direction but mutual positions are irregular from chain to chain. Thus, the packing of the chains is low, leading to the low density. The crystals of PVTfAc are said to be made of helical chains.⁴ When the bulky trifluoromethoxy groups are exchanged

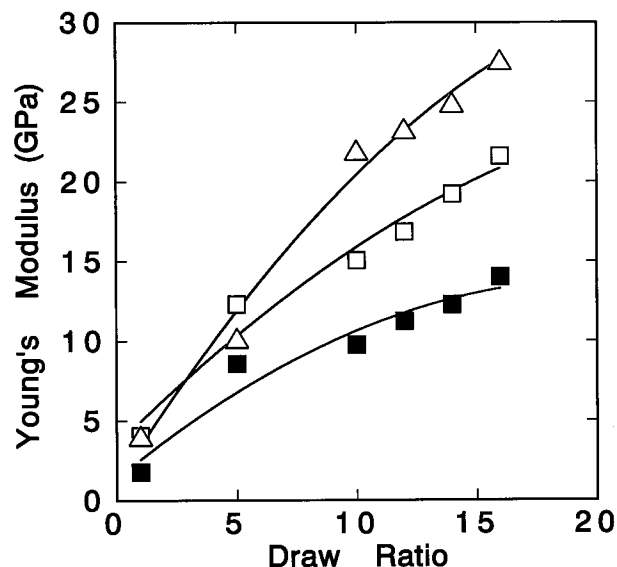


Figure 8 Dependencies of Young's modulus of drawn and saponified (D-S), and saponified and drawn (S-D) PVTfAc on draw ratio: (□) S-59 (D-S); (■) S-64 (D-S); (△) S-59 (S-D).

with small hydrogen atoms and the helical chains are transformed into zigzag chains, crystals with more defects are considered to be formed. The formation of voids is also considered. The melting points of the samples prepared in these experiments are similar to that of the solid prepared from aqueous PVA solution. The crystallization of the samples during heating might be possible. However, it does not seem to occur since the density of the drawn ($\times 13$)/saponified S-59 changed only slightly from 1.296 to 1.305 g/cm³ and the Young's modulus remained unchanged with heating time at 240°C.

Figure 5 shows the variation of the intensity of the infrared absorption band at 1140 cm⁻¹, which is sensitive to crystallization,^{10,11} with the heating time at 200°C. The intensity was independent of the heating time. Figure 6 shows the variation of the s-diad % estimated from the absorbance ratio between those at 916 and 845 cm⁻¹ using the equation¹² $s\text{-diad } \% = 72 \times (D_{916}/D_{845})^{0.40}$ for drawn/saponified and saponified/drawn samples with heating at 200°C. The magnitude of the decrease for the drawn/saponified sample is smaller than that of the saponified/drawn sample. The intensity of the band at 916 cm⁻¹ is reported to decrease with increase of the degree of crystallization.¹³⁻¹⁵ The crystals are suggested to be significantly resistant to heating.

Figures 7 and 8 show the relationship between

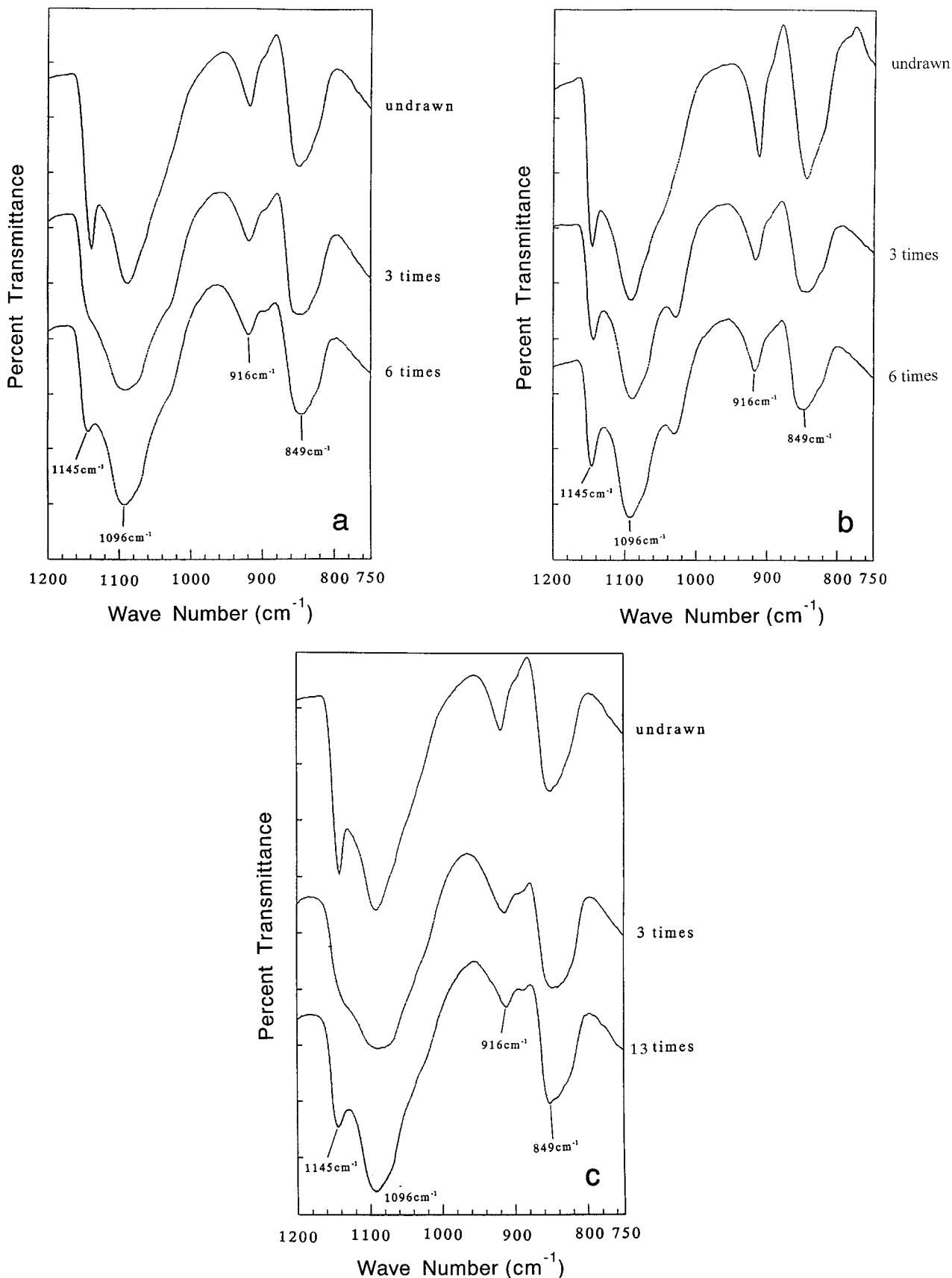


Figure 9 Infrared spectra of drawn and saponified (D-S) and saponified and drawn (S-D) PVTFAC: (a) S-59 (D-S); (b) S-64 (D-S); (c) S-59 (S-D).

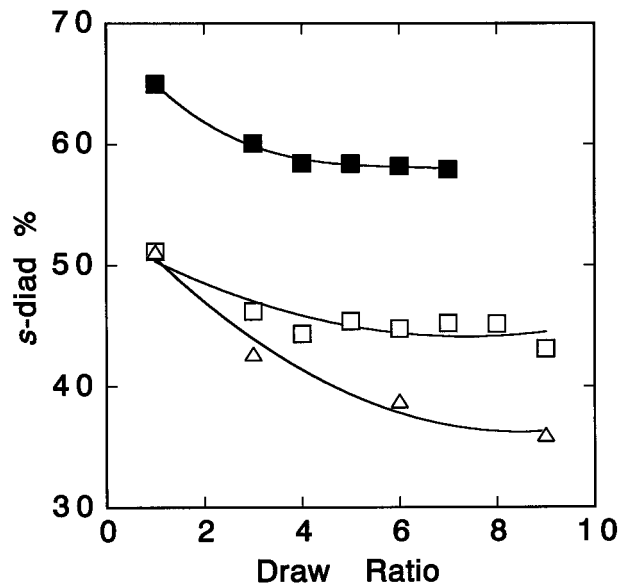


Figure 10 Dependencies of racemic diad contents of drawn and saponified (D-S) and saponified and drawn (S-D) PVTFAC on draw ratio: (□) S-59 (D-S); (■) S-64 (D-S); (△) S-59 (S-D).

the Young's modulus and strength at break. Both increase with increasing draw ratio. This reflects the extension of chains with the drawing. The lower value of the drawn/saponified sample shows a smaller extension of chains than that of the

Table II Dissolution Temperature of Saponified PVTFAC (S-59) Films in Water

Treatment Conditions		Dissolution Temperature (°C)
Before Saponification	After Saponification	
UD		100
UD	HT (200°C)	110
D 4×, HT 1 h		120
D 4×, HT 1 h	HT (200°C)	120

UD: undrawn, D: drawn (100°C), HT: heat treatment (200°C).

saponified/drawn sample at each fixed draw ratio. High-performance films can be prepared by solid-state saponification of drawn PVTFAC. Figure 9 shows the infrared spectra of drawn/saponified S-59 and S-64 and of saponified/drawn S-59. The intensity of the 916 cm⁻¹ band used as a measure of syndiotacticity decreased with an increasing draw ratio. Figure 10 shows the relationship between the apparent s-diad content estimated from the equation described above and the draw ratio. The apparent s-diad % decreased slowly with an increasing draw ratio for drawn/saponified samples and rapidly for saponified/drawn samples. The decrease in the apparent s-diad % with the

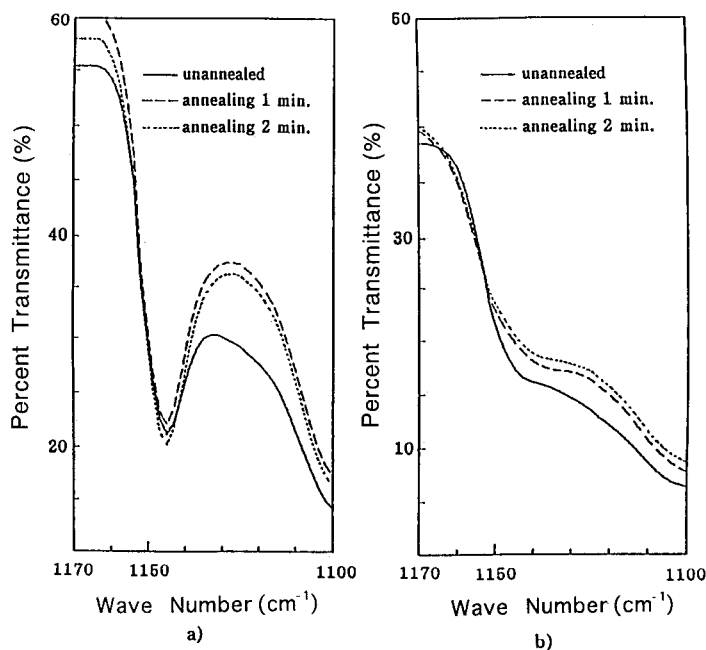


Figure 11 Infrared spectra of heated (180°C) PVA films prepared from aqueous solutions: (a) commercial PVA; (b) S-64.

draw ratio corresponds to the increase in the degree of crystallization. The difference in the magnitude of the decrease is considered to be related to the crystal structure, that is, chain segments in the crystals with more defects contribute to the intensity of the 916 cm^{-1} band.

The estimated s-diad contents are apparent, not true, ones. The true s-diad contents of the samples were previously determined by NMR, as shown in Table I. The reduction of the estimated s-diad contents with the draw ratio is, of course, related to orientation, since the intensity of infrared peaks depends on the direction of the transition moments with respect to the direction axis. Table II shows the dissolution temperatures of the saponified samples. The drawn/saponified samples have a similar hot-water resistance to that of the films from s-PVA.

Finally, we discuss the crystallization-sensitive band at 1145 cm^{-1} in detail. Figure 11 shows the infrared spectra of two kinds of heated PVA films, prepared from aqueous solutions, with degrees of crystallization around 50%. Strong absorption bands at 1145 cm^{-1} are seen. However, Figure 9 shows that the intensities of the bands of drawn/saponified and, moreover, saponified/drawn samples are weak, although those of the samples derived from S-64 are somewhat stronger than are those of the samples derived from S-59. The samples with draw ratios greater than 6 were estimated to have a degree of crystallinity of over 50%. This would be due to the crystal structure characteristic of the samples obtained from this saponification process.

CONCLUSIONS

s-PVA films of low density and high performance were prepared through the saponification of drawn PVTFAC, with gaseous ammonia. PVA molecules are arranged parallel to the draw di-

rection. However, no crystals typical of drawn and heated PVA were made, but those with defects are made. This might be due to the helical arrangement of polymer molecules in drawn PVTFAC.

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