

# Fiber of Poly(vinyl Alcohol) Derived from Vinyl Trifluoroacetate. III. Production and Properties of Fibers

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## Synopsis

The direct wet-spinning of syndiotacticity-rich poly(vinyl alcohol) from ammonolysis solutions of poly(vinyl trifluoroacetate) was carried out. The high draft in spinning could not be accomplished at lower and higher polymer concentration, but it was accomplished at a certain middle polymer concentration. The drawn fibers with high draft have not always high strength. The fibers with high strength were obtained from fibers wound at moderate draft in spinning and then drawn at higher times without solvent. The strength was independent on the degree of polymerization (in a range from DP = 1870 to DP = 5580), but it became higher in the case of thinner fibers obtained from the solutions of lower polymer concentration. Here, the highest Young's modulus and strength at break were 13.8 GPa and 12 gr/denier, respectively.

## INTRODUCTION

The fibers made from commercial poly(vinyl alcohol) (PVA<sub>VAc</sub>), derived from vinyl acetate (VAc), is known as vinyon. The PVA<sub>VAc</sub> dissolves in water at 100°C even if it has high crystallinity due to heating accompanied with drawing. The vinyon improved on the water resistance by formalization has disadvantages such as low hygroscopicity, poor dyeability, etc. Since syndiotacticity-rich PVA (PVA<sub>VTFA</sub>), derived from vinyl trifluoroacetate, does not dissolve in water at 100°C,<sup>1,2</sup> the fiber obtained from PVA<sub>VTFA</sub> is considered to be in water at 100°C in the absence of combined formaldehyde. Now an interesting problem is the production of the fiber with high strength and high modulus which is considered to be made from PVA<sub>VTFA</sub>.<sup>3</sup> The wet-spinning of PVA<sub>VAc</sub> from its aqueous solution is possible, but that of PVA<sub>VTFA</sub> from its aqueous solution is impossible since the solutions gel easily at room temperature.<sup>4,5</sup> The authors have found in a preliminary experiment that the spinning can be carried out from 2,2'-diaminodiethylamine (DTA) solution of PVA<sub>VTFA</sub>.<sup>6</sup> Namely, poly(vinyl trifluoroacetate) (PVTFA) is converted to PVA<sub>VTFA</sub> by dissolving it in DTA. The ammonolysis solutions can be used as solutions for wet spinning. Therefore, the processes of refining and drying PVA<sub>VTFA</sub> and dissolving PVA<sub>VTFA</sub> in water can be eliminated. In this paper the spinning by extruding the ammonolysis solution of PVTFA and the properties of PVA<sub>VTFA</sub> fibers obtained are described.

## EXPERIMENTAL

## Samples

Poly(vinyl trifluoroacetate)s (PVTFA) were obtained by the bulk or solution polymerizations of vinyl trifluoroacetate (VTFA). The Bulk polymerization of VTFA was carried out at 60°C by use of benzoyl peroxide (BPO) as an initiator. The solution photopolymerization of VTFA in tetrahydrofuran (THF) (VTFA/THF = 2/1 v/v) was carried out at temperature of -78°C by ultraviolet light employing 2,2'-azobis(2,4-dimethylvaleronitrile) (ADMVN) as a sensitizer. The degree of polymerization (DP) and the content of syndiotactic diad [*s*-(diad) %] of samples determined according to the methods described previously<sup>7</sup> are shown in Table I.

## Preparation of DTA solution

DTA solutions of PVA<sub>VTFA</sub> were prepared by dissolution accompanied with ammonolysis of PVTFA. The volume ratio of DTA to PVTFA was 5/1. The solutions were centrifuged at the speed of 13,000 rpm to clarify it and then diluted with DTA before spinning.

## Spinning

Figure 1 shows the diagram of the spinning apparatus in which a glass nozzle (the inner diameter of nozzle = 0.175 mm), a first roller, a second roller, a guide roller, and a third roller are arranged in this order.<sup>6</sup> The fiber is elongated between the first and second rollers or the first and third rollers, changing the speeds of them. Methanol was used as a coagulant. In this study, the spinnings were mainly done as follows: the ammonolysis solutions were extruded in methanol from a glass nozzle as a fiber which was wound with a turn on the first roller and then the fiber was wound in air on the third roller after passing through the guide roller. The spinning was carried out at room temperature (about 20°C). The taking-up on the

TABLE I  
Conditions of Polymerization and Properties of Samples

Sample	Conditions of polymerization		Properties	
			DP	<i>s</i> -(diad) %
A	Bulk (60°C)	BPO	1870	54.9
B	Bulk (60°C)	BPO	2370	55.0
C	Bulk (60°C)	BPO	2850	54.2
D	Bulk (60°C)	BPO	4410	57.4
E	Bulk (60°C)	BPO	5580	57.3
F	Photo (-78°C)	ADMVN	1300	64.1

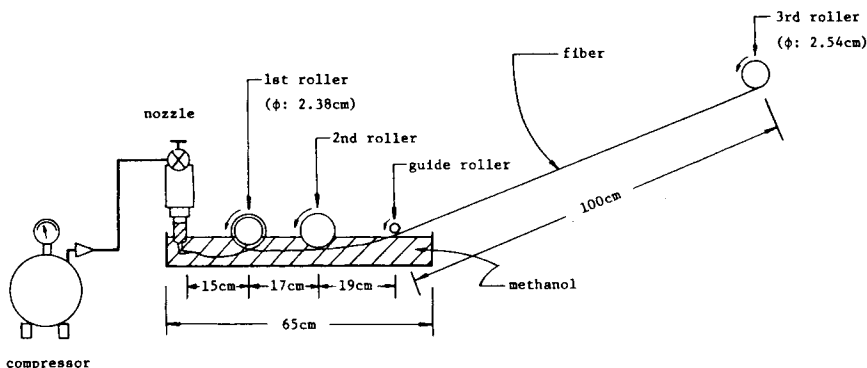


Fig. 1. The diagram of spinning apparatus.<sup>6</sup>

third roller is carried out, moistening fibers always with methanol. The fibers after spinning were stored in methanol.

### Heat Treatment and Elongation

The as-spun 10 fibers were fixed aligning together on the section paper at fiber lengths of 1 or 2 cm. The heat treatment of the fibers without elongation was carried out as follows: Both the ends of the section paper with fibers were fixed by adhesives on a glass plate. The glass plate was inserted in a test tube, and the entrance end of it was covered with aluminium foil. The test tube was immersed in silicone oil maintained at a fixed temperature. The time and temperatures of heat treatment were 10 min and 50, 100, 150, 175, and 200°C, respectively. The elongation of fiber was carried out as follows: The as-spun fibers fixed on the section paper described above were drawn at 100°C in silicon oil, washed with benzene, and heat-treated by the same method shown above.

### Measurements of Fiber Properties

Birefringence was estimated from the retardation obtained using a Sénarmont compensator for a Nikon OPTIPHOT-POL polarizing microscope. Density was determined by the floating method in benzene-carbon tetrachloride mixed solvents. Tensile properties were measured using two tensile testers of a TENSILON UTM-4L type of Toyo-Baldwin Co., Ltd. and TOM/5 type of Shinko Tsushin Kogyo at 20–22°C and a relative humidity of 65%. The length of the fibers was 10 mm for the former tensile tester and 20 mm for the latter one, and the elongation rate was 10 mm/min for the undrawn fibers and 5 mm/min for the drawn fibers. The measurements were carried out for 50 fibers for the same sample, and the Young's modulus and the strength at break are shown as mean values. The wide-angle X-ray diffraction patterns were recorded on a flat film camera for a Rigaku X-ray diffraction apparatus by using nickel-filter  $\text{CuK}\alpha$  radiation.

## RESULTS AND DISCUSSION

### Spinning

The maximum winding rate on the first roller was 2.2 m/min. As the taking-out of the fiber from the first roller was done artificially, the winding rate of 2.2 m/min was the upper limit in this experiment. Therefore, the draft between the nozzle and the first roller was nearly zero, and the fibers obtained among them showed only faint birefringence. Figure 2 shows a polarizing micrograph for the fibers obtained between the nozzle and the first roller. When the fiber taken out from the first roller was wound on the second roller, the maximum draft among them was about 3. Even if the fibers obtained were stored in methanol for few weeks, the considerable amounts of solvent remained in fibers. Therefore, the fibers wound round on the second roller adhered to each other in drying in air. (Fig. 3)

Table II shows the relation between the spinning conditions and deniers for samples A, B, D, E, and F. In the case of same concentration, the solution viscosity increases with increasing in molecular weight. Therefore, when the speed of the first roller is same, the higher pressure is necessary for the sample with higher molecular weight. The sample with higher molecular weight coagulates easily, though the coagulation occurs only in the neighborhood of surface of fiber. Therefore, the draft between the first and third rollers must be held lower in order to resist the winding force to the third roller and the fibers obtained become thicker. In the case of sample F, the polymer concentration of solution and the denier of fiber are higher

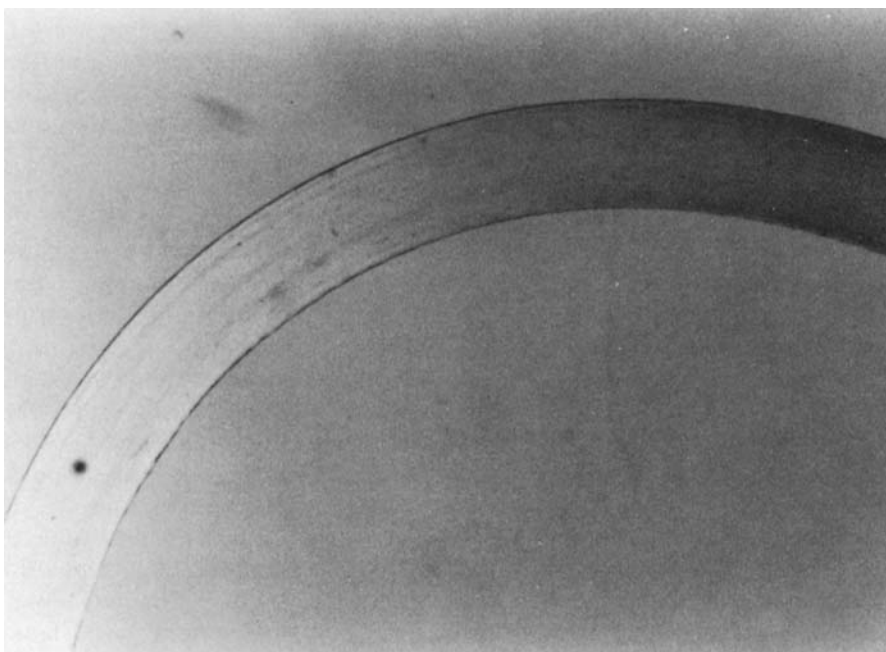


Fig. 2. Polarized optical micrograph for PVA<sub>VTFA</sub> fiber obtained between the nozzle and the first roller. The fiber contains solvent and is immersed in methanol.



Fig. 3. Optical micrograph for PVA<sub>VTF</sub> fibers obtained winding on the second roller. The fibers were dried on the second roller.

than that of other samples. Sample F has higher syndiotacticity than that of sample A–D. The PVA with higher syndiotacticity has a higher ability of coagulation as well as the PVA with higher molecular weight.

When the draft between the first and third rollers came over three times, the fibers superposed did not adhere to each other even after drying. An aim in this experiment is to obtain fibers with higher strength. Accordingly, the higher orientation of polymer chain in fiber is necessary, that is, it is profitable to give higher draft. Table III shows the relation between spinning condition and denier for sample B. As shown in Table III, the draft was the highest at the polymer concentration of 4.76 g/dL for sample with DP = 2370. When the polymer concentration of spinning solution becomes high, the fibers obtained become thick because of the prevention of the penetration of methanol molecules to fibers. When the polymer concentration of spinning solution becomes low, the fibers obtained become thin. Accordingly, in the case of both fibers obtained from the solutions with higher or lower polymer concentration, the winding force to the third roller is low, so that the draft was the highest at a certain polymer concentration because of the easy breaking of fibers with solvent by the low coagulation for the solution with high concentration and the formation of thin fibers for that with low concentration. The fiber of low denier could be obtained by extruding the solution with low concentration under low pressure. As shown in Table II, for the sample F (high syndiotacticity content) the fiber with high denier was obtained under this spinning condition due to the rapid coagulation at the surface. Since it seems that the fiber with higher strength can be obtained from PVA of higher syndiotacticity, the spinning for PVA with high syndiotacticity should turn toward the research on how to make the fiber with low denier.

TABLE II  
The Spinning Conditions and Denier of Fibers

Sample	Experimental times	Concentration (g/dL)	Pressure (Kg/cm <sup>2</sup> )	Roller speed (m/min)			Draft	Denier
				1st	3rd	3rd		
A	9	1.62-4.57	0.5-3.0	1.07-1.90	3.45-7.41	1.89-4.87	0.87-2.51	
B	12	3.76-4.94	0-3.0	0.99-1.87	4.36-9.00	3.08-4.99	2.56-6.00	
D	14	2.37-6.33	0.5-4.0	0.76-2.20	2.91-9.30	2.37-5.50	0.92-5.08	
E	22	2.34-3.53	0.5-5.0	0.42-0.96	1.15-4.50	2.39-5.33	1.06-13.5	
F	5	5.25-6.72	2.5-3.0	0.67-1.03	3.64-5.15	4.43-5.76	7.81-13.0	

TABLE III  
The Relation between Spinning Conditions and Deniers of Fibers for Sample B

Concentration (g/dL)	Pressure (Kg/cm <sup>2</sup> )	1st roller speed (m/min)	Draft	Denier
4.94	3.0	0.989	4.61	5.93
4.76	3.0	1.42	4.92	4.66
4.51	2.5	1.33	4.87	4.55
4.51	2.0	0.996	4.41	5.29
3.97	1.5	1.39	4.34	3.79
3.76	1.5	1.74	4.10	3.64

### Properties of Fibers

At first, the effect of the molecular weight on Young's modulus and the strength of fibers is shown. Table IV shows the spinning conditions and properties of fibers obtained for four samples with different molecular weights. Those fibers have roughly resemble denier. Figure 4 shows stress-strain curves of a bundle of undrawn 10 fibers for four samples annealed at 50°C. The stress-strain curves have clear stairlike curves. This shows that the untreated as-spun fibers are significantly nonuniform. Although the stress-strain curves of as-spun fibers have a plateau part similar to untreated PVA<sub>VTFA</sub> films,<sup>3</sup> it is due to the necking of fiber in drawing. Although the untreated PVA<sub>VTFA</sub> film had a maximum stress at the yield point in the stress-strain curves, the stress of plateau parts in the stress-strain curve for the untreated as-spun PVA<sub>VTFA</sub> fiber was higher than that at the yield point. The difference is due to the orientation of polymer chains in the materials, that is, the polymer chains for the former are unoriented, but for the latter somewhat oriented. Figure 5 shows the stress-strain curves for fibers drawn at 100°C in silicon. The drawing of fibers at 100°C in silicon was stopped immediately before breaking. The limited draw ratio at 100°C was influenced by the polymer concentration, the speed of the first roller, and the drafting spinning, but the effect of the molecular weight on the drawing of as-spun fiber was unclear. The reason for difference in each curves in Figure 4 is unclear, whereas it is clear in Figure 5. The drawn fibers of samples B and D are still uniform. The spinning solutions of samples B and D had higher polymer concentration than that of samples A and

TABLE IV  
The Spinning Results and Properties of Fibers

Sample	Concentration (g/dL)	Draft	Denier	Birefringence $\Delta n \times 10^5$	Draw ratio at 100°C in silicon oil	Total draw ratio
A	2.73	4.29	2.02	8.65	3.79	16.26
B	3.97	4.50	2.56	5.35	2.49	11.21
D	3.89	5.50	2.60	4.24	1.54	8.47
E	2.95	4.19	2.90	5.76	2.67	11.19

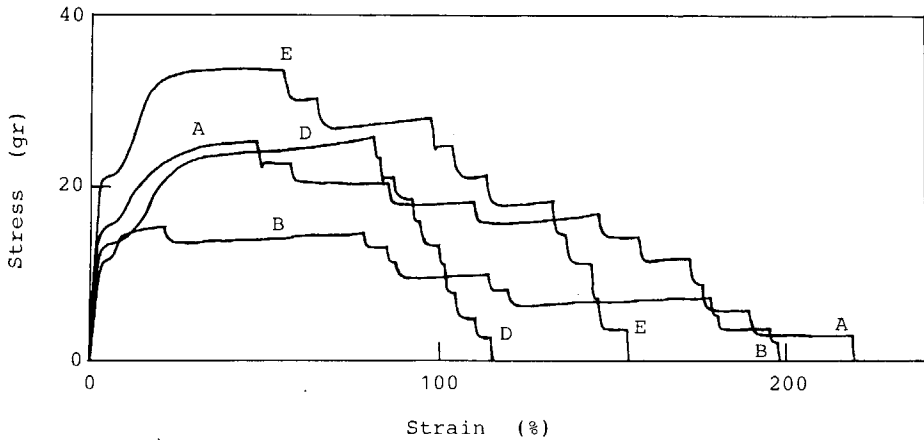


Fig. 4. Stress-strain curves of a bundle of PVA<sub>VTFA</sub> 10 fibers rolled on the third roller (A: sample A, 2.02 denier  $\times$  10; B: sample B, 2.56 denier  $\times$  10; D: sample D, 2.60 denier  $\times$  10; E: sample E, 2.91 denier  $\times$  10). The fibers were annealed at 50°C for 10 min.

E. Although the drafts of the former were higher than that of the latter, the limited draw ratios, Young's modulus, and the strength at break were the opposite (Tables IV and V). Figure 6 shows the relations between Young's modulus and the annealing temperature, and Figure 7 shows the relation between the elongation at break and the annealing temperature for undrawn and drawn fibers of samples A and D. The elongation at break for the undrawn fibers prepared from the solutions with lower polymer concentration was greater than that for the undrawn fiber prepared from the solutions with higher polymer concentration, and, for the drawn fibers prepared from the solutions with lower polymer concentration, it was smaller than that for the drawn fibers prepared from the solutions with higher

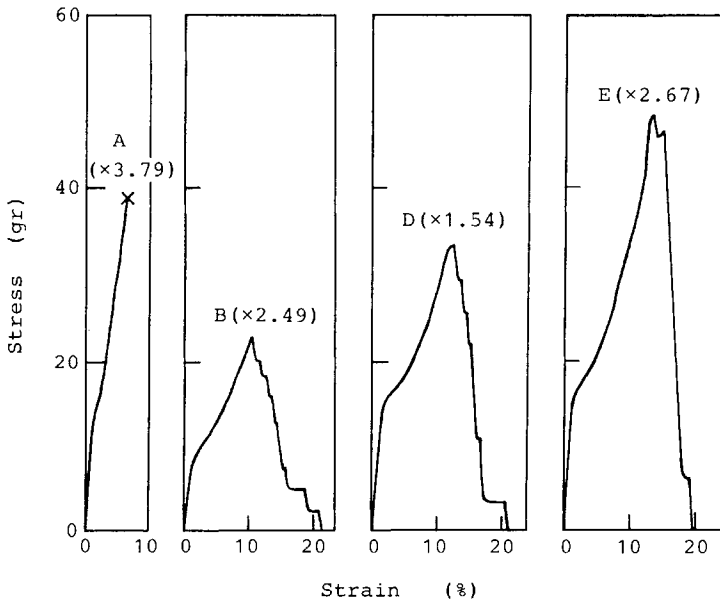


Fig. 5. Stress-strain curves of a bundle of PVA<sub>VTFA</sub> drawn and annealed (at 100°C in silicon) 10 fibers. Samples are same that shown in Figure 4. Numbers in brackets are draw ratios.



TABLE V  
Properties of Fibers (Continued from Table IV)

Sample	Concentration (g/dL)	Young's modulus (GPa)		Strength at break (GPa)	
		As-spun fiber annealed at	Drawn fiber annealed at	As-spun fiber annealed at	Drawn fiber annealed at
		50°C	200°C	50°C	200°C
A	2.73	1.23	6.40	0.100	0.235
B	3.97	1.02	2.38	0.0562	0.0799
D	3.89	0.97	1.85	0.0445	0.0628
E	2.95	1.43	4.66	0.0845	0.180

polymer concentration. As described in the previous section, this is influenced by the degree of penetration of methanol molecules to the interior of fiber, that is, the whole as-spun fibers prepared from the solutions with lower polymer concentration have higher uniformity of chain orientation. Therefore, the drawn fibers prepared from the solutions with lower polymer concentration had higher Young's modulus (see Fig. 6).

As we reached a conclusion that the fibers prepared from the solutions with low polymer concentration have high modulus, we carried out the tensile test for the fibers shown in Table VI. From Tables IV and VI, the birefringence of as-spun fiber prepared from the solutions with low polymer concentration is recognized to be higher than that from the solutions with high polymer concentration, but the draw ratio is reversely. Figure 8 shows stress-strain curves of elongated and heat-treated ( $T_{\text{ann}} = 100^\circ\text{C}$ ) fibers for sample A shown in Table IV (A-1 in Fig. 8) and Table VI (A-2 in Fig. 8). Both of samples had similar stress (g) at break, whereas the strength at break and the yield point for sample A-2 were remarkably high in contrast to those for sample A-1. Table VII shows the strength at break and Young's

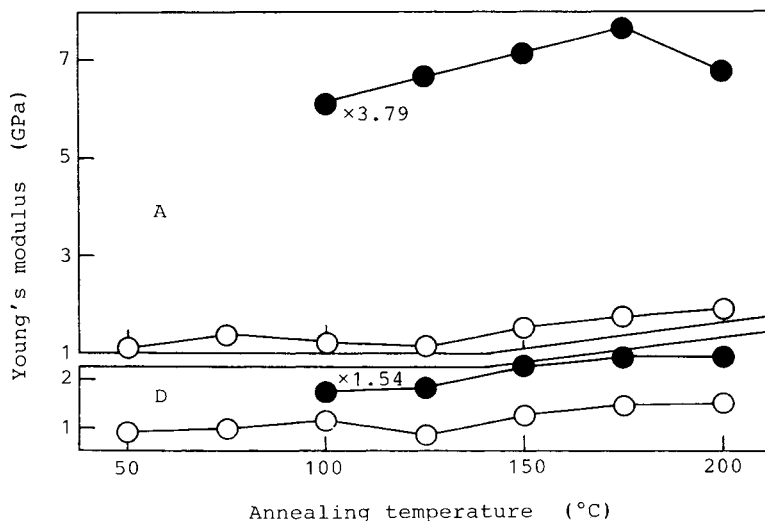


Fig. 6. Relations between the Young's modulus and the annealing temperature for PVA<sub>VTFA</sub> undrawn and drawn fibers of sample A and D. Numbers in the figure are draw ratios.

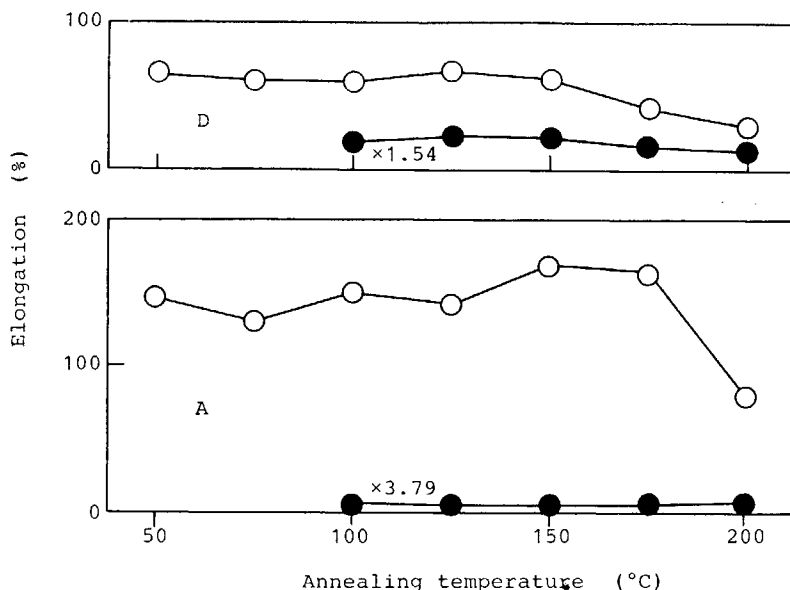


Fig. 7. Relations between the elongation and the annealing temperature for PVA<sub>VTFA</sub> undrawn and drawn fibers of sample A and D. Numbers in the figure are draw ratios.

modulus of fibers shown in Table VI. Table VII shows that the maximum Young's modulus of commercial vinylon is 30 GPa, but Young's modulus and the strength at break for common commercial vinylon are below 10 GPa and below 10 g/denier, respectively. Those values of PVA<sub>VTFA</sub> fibers shown in Table VII were higher than those of common commercial vinylon. The elongated and heated (at 200°C) fibers of PVA<sub>VTFA</sub> were insoluble at 100°C in water; thus we could prepare the boiling water resisting vinylon without formaldehyde and with high strength.

Figure 9 shows the X-ray diagrams of fibers described in Table VIII. Although the draft of as-spun fibers was considerably high, the X-ray diagrams showed only Debye-Scherrer rings [Fig. 9(a)]. Even the fibers unelongated and heated under constant length at 200°C showed only Debye-Scherrer rings [Fig. 9(b)]. The poor orientation of polymer chains in the as-spun and annealed fibers is also recognized from the result of birefringence (see Table VIII). Although the PVA<sub>VAc</sub> fibers heated at 200°C could not resist the boiling water, the as-spun PVA<sub>VTFA</sub> fibers heated at 200°C had the stability for boiling water. Although the difference in the degree of crystallization for both of PVA fibers was slight, the stability for boiling water differed extremely. The authors have recognized by X-ray analysis

TABLE VI  
The Spinning Results and Properties of Fibers for Sample A Which Have Highest Modulus in This Experiment

Sample	Concentration (g/dL)	Draft	Denier	Birefringence $\Delta n \times 10^5$	Draw ratio at 100°C in silicon oil	Total draw ratio
A	1.62	4.84	0.869	16.6	3.00	14.52

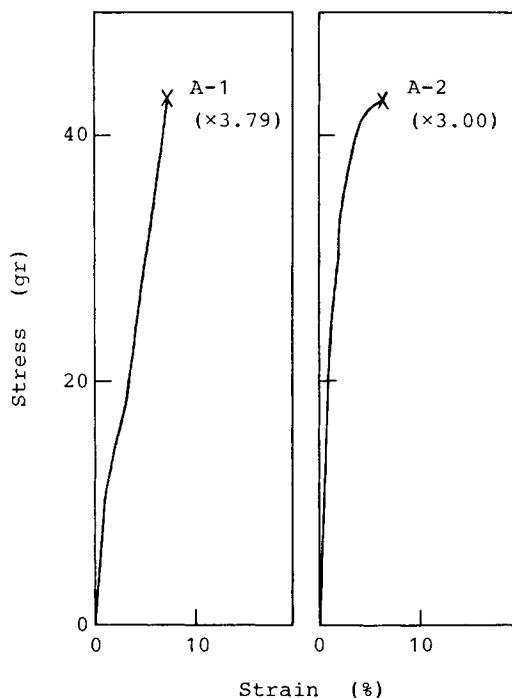


Fig. 8. Stress-strain curves of a bundle of PVA<sub>VTFA</sub> drawn and annealed (at 100°C in silicon) 10 fibers (A-1: sample A, 2.02 denier  $\times$  10; A-2: sample A, 0.869 denier  $\times$  10). Numbers in the figure are draw ratios.

that the linear thermal expansion coefficient for crystals for PVA<sub>VTFA</sub> were smaller than those in PVA<sub>VAc</sub>.<sup>8</sup> The crystallites of PVA<sub>VAc</sub> have been considered to be formed with the intermolecular hydrogen bonds between the hydroxyl groups arranged randomly along PVA molecules.<sup>9</sup> Recently it has been found that the crystallites had the intramolecular hydrogen bonds other than the intermolecular hydrogen bonds and the content of the former decreased with increasing syndiotacticity of PVA.<sup>10</sup> Therefore, the higher intermolecular hydrogen bond content in PVA<sub>VTFA</sub> in comparison with that

TABLE VII  
Properties of Fibers (Continued from Table VI)

Sample	Concentration (g/dL)	Young's modulus (GPa)		Strength at break			
		As-spun fiber annealed at 50°C (GPa)	Drawn fiber annealed at 175°C (GPa)	As-spun fiber annealed at 50°C		Drawn fiber annealed at 175°C	
				(GPa)	(g/denier)	(GPa)	(g/denier)
A	1.62	8.18	13.78	0.210	3.98	0.507	11.9
Commercial vinylon	—	—	3-30	—	—	—	3-10

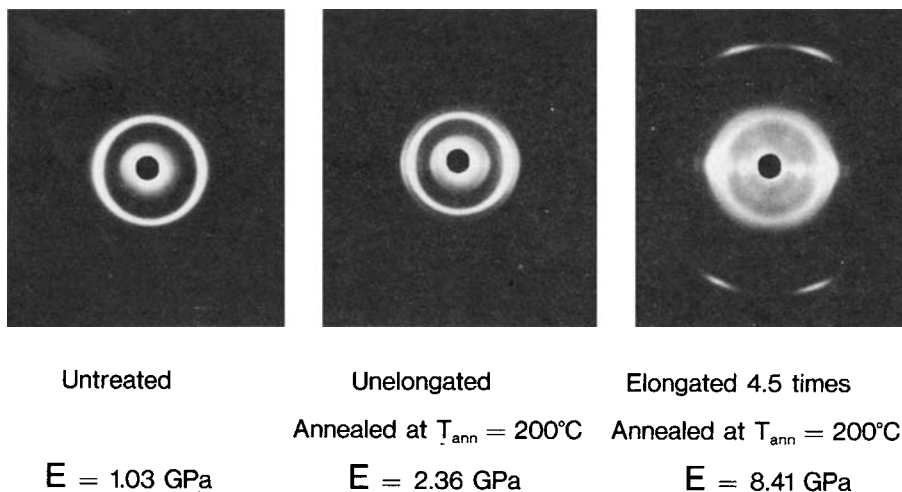


Fig. 9. Wide angle X-ray diffraction patterns of fibers for sample C described in Table VIII.

in  $PVA_{VAc}$  is considered to be the reason for the stability of the crystallites for  $PVA_{VTFA}$ , thus for the stability and the strength of  $PVA_{VTFA}$  fibers.

### CONCLUSIONS

In this paper, the direct wet spinning of syndiotacticity-rich poly(vinyl alcohol) from the ammonolysis solution of poly(vinyl trifluoroacetate) was carried out using the spinning apparatus shown in Figure 1, the most suitable condition of spinning was selected, and the strength of fibers obtained was examined. From those results, we obtained the following conclusions:

1. The draft between the nozzle and the first roller is nearly zero and the maximum winding rate on the first roller was 2.2 m/min.
2. When the draft between the first and third rollers came over three times, the fibers superposed did not adhere to each other even after drying.
3. The most suitable condition of spinning was subject to the solution viscosity and the coagulability of polymer.
4. In this experiment, the maximum winding speeds were 2.2 m/min on the first roller and 9.30 m/min on the third roller, respectively, and the maximum draft between both the rollers was 5.76.
5. The fibers with high strength were obtained from fibers wound at moderate draft in spinning and then drawn at higher times without solvent.

TABLE VIII

The Spinning Results and Properties of Fibers used of the Preparation of X-Ray Diagrams (Fig.9)

Sample	Concentration (g/dL)	Roller speed (m/min)		Draft	Denier	$\Delta n \times 10^5$
		1st	3rd			
C	3.29	1.12	5.98	5.34	2.61	6.10

6. The maximum Young's modulus and strength at break for drawn/annealed fiber obtained in this experiment were 13.8 GPa and 12 g/denier, respectively.

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