Melt Spinning of Syndiotactic 1,2-Polybutadiene for Preparation of Carbon Fibers

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Synopsis

The thermal crosslinking and loss of vinyl unsaturation of syndiotactic 1,2-polybutadiene(s-PB) at 180–230°C were prevented by stabilizers with 3,5-di-*t*-butyl-4-hydroxybenzyloxy group. The s-PB samples (mp 140–198°C and MW 20,000–70,000) that contained the stabilizers could be melt-spun at a temperature below 220°C into 1-denier fibers to be used for the preparation of carbon fibers. The s-PB fibers with higher mp and/or higher MW could be obtained by the addition of a high boiling solvent such as tetralin. The relationship between the molecular structures of s-PB and the properties of resulting s-PB fibers, including the degree of molecular orientation measured by birefringence and x-ray diffraction, is presented. Spun fibers showed small swellings here and there along the fiber axis, which would have resulted from the inhomogeneity of the melt of s-PB spun at a temperature slightly above the melting point. The gelation was unlikely to occur.

INTRODUCTION

The synthesis of highly crystalline syndiotactic 1,2-polybutadiene (henceforth abbreviated s-PB) was described in an earlier article.[1] Because of its high reactivity and high carbon content s-PB would be a promising raw material for carbon fibers[2] if it could be spun into fine filaments. However, we have found it difficult to form the melt of s-PB into filaments because of the sensitivity of s-PB to thermal degradation. In fact, there is scarcely any literature relating to melt spinning of any kinds of syndiotactic 1,2-polybutadiene. For the production of high-quality carbon fibers fine precursor filaments with a diameter below 20 μm and a high uniformity and high degree of molecular orientation are essential.[3] The purpose of this study is to make s-PB resistant to thermal degradation by the use of pertinent stabilizers to permit melt spinning at high temperatures. The effect of the stabilizers and the properties of melt-spun fibers is interpreted in terms of the molecular structure.

EXPERIMENTAL

Materials

The synthesis[1] and characterization[4] of s-PB have been reported elsewhere. Commercial stabilizers and a fatty acid diethanolamide (Dianol 300, made by Daiichi Kogyo Seiyaku K.K. Japan) were used without further purification. Amides and compounds with 2,6-di-*t*-butyl-4-hydroxybenzyloxy group were prepared in the usual way and all products gave satisfactory analyses.

Test Method of Heat Stabilizer

A stabilizer was blended with powdery s-PB in a swollen state by the use of 5–7 times the chloroform in volume per unit weight of polymer. This mixture was dried *in vacuo* at a temperature below 45°C. The blend (1.5 g) was mixed in a melt indexer with a nozzle 0.5 mm in diameter and an *L/D* (length/diameter) of 16 at 205°C for 1 min. After deaeration by sudden pressure the polymer melt was maintained in it. Melt-viscosity (ηt) was measured at 205°C with the melt indexer after heat treatment for t min.

INFRARED

Infrared (IR) spectra were obtained by the KBr-disk method. The content of vinyl groups (%) was calculated by eq. (1):

$$\text{Content of vinyl groups (\%)} = \frac{D/w}{(D/w)_0}, \tag{1}$$

where D = absorbance at 907 cm^{-1}, w = sample weight (mg) in KBr-disk, $(D/w)_0$ = absorbance of s-PB with vinyl content of 100%/1 mg.
$(D/w)_0$ was calculated from the corrected values by ^{1}H-NMR[4] of s-PB with mp 188–205°C. To obtain a reproducible value it is necessary to grind strongly by hand for more than 30 min (Fig. 1). Grinding by vibrator[5] was too weak to disperse s-PB into a KBr matrix. Sample weight (w) in a 200-mg KBr-disk ranged from 0.2000 mg for s-PB to 2.000 mg for a heat-treated sample with lower vinyl content.

Vinyl content by this method of s-PB with a mp lower than 170°C was smaller than that anticipated by ^{1}H-NMR measurement. The polymer was not finely dispersed in KBr because of its softness; therefore the intensity was low.[6] The heat-treated sample hardens because of cyclization and crosslinking after initial softening due to the decrease in crystallinity as the vinyl contents decrease.

Tanaka et al.[7] reported that high vinyl PB had greater absorbance than that anticipated by lower 1,2-PB. In this article high vinyl PB was chosen as the standard, but the true value of the vinyl content of heat-treated species may be somewhat higher.

Orientation

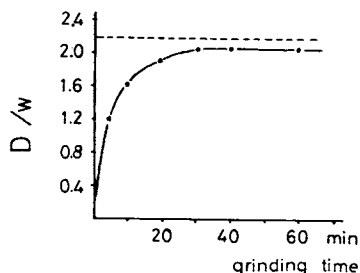Crystalline orientation was measured by scanning the reflection intensity

Fig. 1. Absorbance D at 907 cm^{-1} per sample weight w (mg) in KBr disk versus grinding time. The dotted line shows the value of the absorbance with vinyl-content of 100% per 1 mg, $(D/w)_0$.

distribution of (010) along the arc. Orientation parameter $W(\%)$ was calculated by eq. (2):

$$W(\%) = \frac{180 - H_{1/2}}{180} \times 100 \qquad (2)$$

where $H_{1/2}$ = the half-intensity width of (010).

The birefringence (Δ) of the fibers was determined with a Nikon polarizing light microscope equipped with a Berek compensator.

Mechanical Properties

The mechanical properties of the melt-spun fibers were measured at room temperature with an Instron tensile tester at a crosshead speed of 5 mm/min and an initial fiber length of 20 mm.

Glass Transition Temperature

Glass transition temperature is the peak temperature of tanδ which was measured by Rheovibron dynamic viscometer (model DDV-II) at a frequency of 110 Hz and a constant rate of heating (1°C/min).

Melt Spinning

A polymer blend was prepared by mixing 100 parts of s-PB, 1 part of 3,5-di-t-butyl-4-hydroxybenzylalcohol, and 1.5 parts of 3,5-di-t-butyl-4-hydroxytoluene with chloroform; the mixture was dried *in vacuo* below 45°C. The blend was melt-spun in two types of procedure:

(1) The blend (1.5 g) was melt-spun into a monofilament by using a melt indexer with a spinneret of 0.4 or 0.5 mm in diameter and $L/D = 16$. As-spun fibers were drawn with a hand stretching machine at a rate of 100%/min in water at 50°C.

(2) The blend (>500 g), which was extruded at 205°C in hot water (60–80°C) to be pelletized, was melt-spun with a Shimazu spinning apparatus fitted with a 20-mm diameter screw and a spinning head. The nozzle had a diameter of 0.35 mm, $L/D = 3$, and 40 holes. Filament bundles were drawn over warm water at a stretching rate of 100%/min in a continuous drawing machine and a heat-treatment bath of about 2 m.

The extrusion temperature was kept constant at 205°C. The polymer was extruded at a rate of about 0.15 g/min, and filaments were produced at a speed varying between 100 and 800 m/min.

RESULT AND DISCUSSIONS

Heat Stabilizer

Melt viscosity increased because of crosslinking when s-PB was maintained above 180°C without a heat stabilizer. Table I and Figure 2 show the anticrosslinking effect of stabilizers on s-PB in limited contact with air in terms of the ratio of the increased viscosity of melt after heat treatment at 205°C in a melt indexer to the uncrosslinked polymer. Similar data were obtained for the

TABLE I
Heat Stabilizer for Syndiotactic 1,2-Polybutadiene

Type	Stabilizer
Very effective	HO—(ring)—CH$_2$O—X (—X = —H, —COCH$_3$, —COCH=CH$_2$, —COPh, —CH$_3$, —CH$_2$NHCOCH=CH$_2$, —) (di- or triethanolamine acceralates the effects)
Effective A ~ B	HO—(ring)—CH$_3$ + amide containing long conjugative group
Small effect B ~ C	HO—(ring)—CH$_3$, HO—(ring)—CH$_2$—(ring)—OH, (ring)—CH$_2$—(ring with OH, OH)
No effect D	HO—(ring)—CHO, HO—(ring)—CO—(ring), (ring)—NH—(ring)—NH—(ring), (naphthyl)—NH—(ring)—NH—(naphthyl) (HO—(ring)—CH$_2$CH$_2$COOCH$_2$)$_4$C, HO—(ring)—NH—(triazine: N=, N, O—(ring)—OH, SC$_8$H$_{17}$) (OH ring)—CH$_3$ CH$_3$—(OH ring)—S—, (OH ring)—CH$_2$—(OH ring) with CH$_3$ CH$_3$ HO—(ring), HO—(ring)CH$_2$CH$_2$COOC$_{18}$H$_{37}$

a A, B, C, D is shown in Figure 2.

measurement of anticrosslinking effect in an atmosphere of nitrogen. Stabilizers with 3,5-di-t-butyl-4-hydroxybenzyloxy group (BZO) are effective for preventing thermal crosslinking of syndiotactic 1,2-polybutadiene.

Anticrosslinking reagents: HO—(ring)—CH$_2$O—X   BZO-X

X = H, alkyl, aryl, acyl, acryl,
acrylaminomethyl
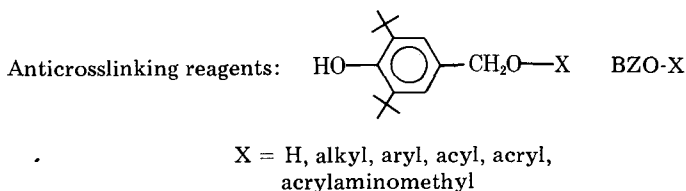
The stabilizers BZO-X appear to be somewhat specific in their ability to prevent the heat-degradation of s-PB. Tetrakis[methylene-3(3,5-di-t-butyl-

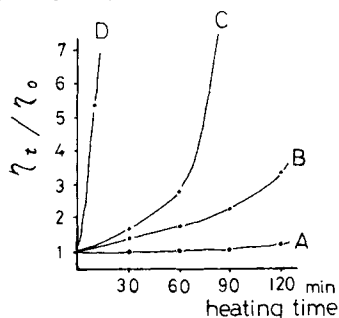| Curve	Stabilizer	Parts per 100 parts polymer
A	3,5-di-t-butyl-4-hydroxybenzylalcohol(1) + triethanolamine(1)	
B	p-methoxycinnamicstearylamide(1) + 3,5-di-t-butyl-4-hydroxytoluene(1)	
C	3,5-di-t-butyl-4-hydroxytoluene(1)	
D	3,5-dimethyl-4-hydroxytoluene(1)	

Fig. 2. Ratio of melt viscosity of s-PB blended with the stabilizers versus heating time at 205°C in a melt-indexer

4-hydroxyphenyl)-propionate] methane (Irganox 1010), and aromatic amines are ineffective; the former is an excellent stabilizer for PE and PP and the latter, for diene elastomers. 3,5-Di-t-butyl-4-hydroxybenzylalcohol (X=H) and 3,5-di-t-butyl-4-hydroxybenzylacrylate (X=COCH=CH$_2$) are rather unsatisfactory antioxidants for rubber.[8] Irganox 1010 prolonged the induction period during the oxidation of s-PB at a temperature of 140–170°C much longer than BZO-H. A stabilizer system composed of 3,5-di-t-butyl-4-hydroxytoluene (BHT) and amides with long conjugative group protected the crosslinking of s-PB, although the effect was relatively small. The order of decreasing effectiveness is as follows:
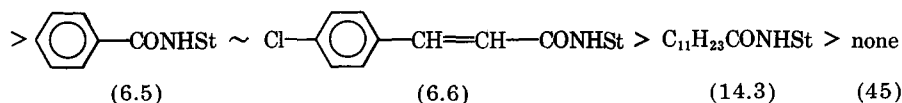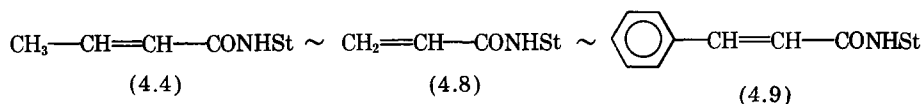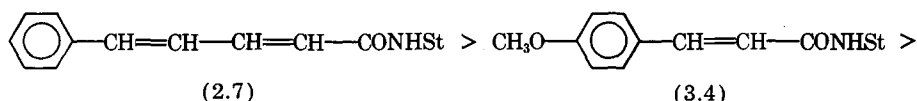
St = stearyl group

$$(\ ) = \eta_{120}/\eta_0$$

The ratio of melt viscosity after heat-treatment for t min to ungelled polymer, η_t/η_0, was also dependent on the procedure of de-ashing from the polymer made with Co(acac)$_3$-AlEt$_3$-CS$_2$ catalyst. The de-ashing with hydrogen chloride and methanol that contained BHT under nitrogen, followed by the precipitation and washing with methanol and a small amount of BHT gave better results; that is, a lower value of η_t/η_0.
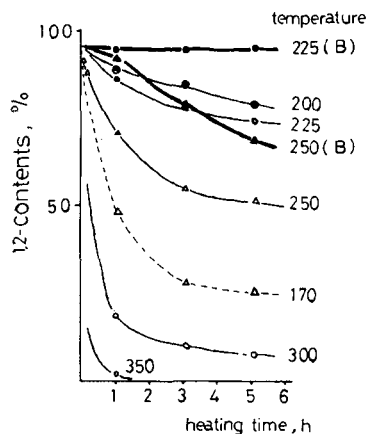
Fig. 3. Changes in the contents of vinyl with (B) or without anticrosslinking agents (no mark) during heat treatment in the temperature range 200–350°C in nitrogen (—,-) and in air (- - - - -) (B) is a blend of s-PB with MP 190°C (100 parts) and 3,5-di-t-butyl-4-hydroxybenzylacrylaminomethyl-ether(1) and Dianol 300(1).

Figure 3 shows that a decrease in vinyl content during heat treatment at 225°C in an atmosphere of nitrogen can be prevented by compounding the stabilizers. The contents of vinyl groups decreased by heat treatment at 250°C in spite of compounding the stabilizer. The vinyl loss observed for 250°C, (B) in Figure 3, is partly due to the decomposition of the stabilizers. BZO—CH$_2$NHCO-CH=CH$_2$ decomposed rapidly at 250°C in nitrogen or *in vacuo*. The main decomposition product *in vacuo* was 3,5-di-t-butyl-4-hydroxybenzaldehyde, which was obtained as a sublimate and has no effect on the stabilization, as Table I shows. In a blend of 100 parts s-PB, 1 part BZO-H, and 1.5 parts BHT 85% of the vinyl content remained after heat treatment at 250°C for 4 h.

Although the mechanism of the stabilization is not made clear, a description is presented below.

Grassie and Heaney proposed a nonradical mechanism for vinyl loss and crosslinking in a thermal degradation study at 200–250°C on PB with 9–14% vinyl groups.[9] Their conclusion was based principally on the fact that the vinyl loss curves were comparable to those in the presence of typical free-radical inhibitors: diphenyl-picrylhydrazyl, 1,4-diaminoanthraquinone, and 2,2-methylene-bis(4-ethyl-, 6-t-butyl-phenol) (MBP). The results of the effect of BZO-X on preventing the crosslinking and a decrease in vinyl double bonds of s-PB require the reinvestigation of the nonradical mechanism of thermal degradation of PB.

It was confirmed by IR spectroscopy that the IR spectra of heat-degraded polymer resemble those of the polymer cyclized by cationic or radical species and that the loss of double bonds in s-PB is accompanied by substantial methyl production, found by Golub and Sung for various polybutadienes.[10] However, cationic species are unlikely to act because of the ineffectiveness of aromatic amine.

There is some evidence that implies a radical mechanism for the stabilization of s-PB with BZO-X. The vinyl double bonds of s-PB reacted with the oxyradical initiator of the hydrogen abstracting type, such as 2,5-dimethyl-2,5-bis(t-

TABLE II
Mechanical Properties of the Syndiotactic 1,2-Polybutadiene Fibers[a]

	Polymer			Properties of Drawn Fibers				
No.	Mp (°C)	T_g (°)	ηa[b] (P)	Diameter (μ)	Elongation (%)	Initial modulus (t/cm^2)	Tensile strength (t/cm^2)	Bire-fringence ($\times 10^{-3}$)
1	152	11	713	12.1	20.9	5.98	3.38	−10.8
2	167	19	784	10.5	17.5	12.2	3.68	−12.7
3	170	21	724	11.8	16.7	15.9	3.52	−12.1
4	179	26	1020	12.5	13.7	27.6	3.28	−13.7
5	187	30	592	11.1	19.1	16.6	2.21	−13.1
6	190	31	470	11.4	11.2	33.0	3.8	−14.0
7	192	33	373	14.0	18.3	16.7	1.61	−13.6
8	195	34	497	12.0	16.7	21.7	2.21	−14.2
9	198[c]	35	8200	13.9	11.2	25.6	1.7	−12.5

[a] The fibers were melt-spun by the use of melt indexer.
[b] ηa = apparent melt-viscosity.
[c] A mixture of polymer blend and tetralin (50:50 by weight) was melt-spun. The apparent melt viscosity of the mixture at 205°C was 620 p. As-spun fibers were drawn after washing with n-hexane and drying in vacuo.

TABLE III
Properties of Undrawn Syndiotactic 1,2-Polybutadiene Fibers[a]

No.	Polymer			Diameter (μ)	Elongation (%)	Tenacity (t/cm^2)	Initial modulus (t/cm^2)	Orientation	
	Mp (°C)	ηa (p)						W %	Δn $\times 10^{-3}$
1	189	188		—	—	—	—	74.2	−6.5
2	192	373		—	—	—	—	75.8	−8.8
3	192	451		—	—	—	—	78.0	−8.8
4	187	592		19	202	0.98	5.4	77.6	−8.7
5	193	439		18.3	217	0.94	7.0	76.4	−8.9
6	185	1350		18.6	134	1.1	8.9	84.9	−11.8
7	192	1430		17.1	110	1.2	10.8	84.8	−11.7
8	181	1270		16.9	109	1.1	7.8	84.7	−10.7
9	187	1985		17.0	106	1.3	9.8	86.0	−11.7

[a] The fibers were melt-spun by the spinning apparatus with a 20-mm screw.

TABLE IV
Crystallization Data for Syndiotactic 1,2-Polybutadiene

No.	Mp (°C)	ηa (P)	Crystalli- zation temperature (°C)	Abrami No. (n)	Rate constant (k)	Half-time of crystalli- zation, $t_{1/2}$ (min)
1	185	1350	163	2.43	1.32×10^{-5}	1.46
			166	2.57	4.67×10^{-7}	4.2
			168	2.51	8.17×10^{-8}	9.6
2	192	1430	171	2.50	2.08×10^{-6}	2.7
			174	2.59	9.99×10^{-8}	7.2
3	181	1270	157	2.14	2.75×10^{-5}	1.9
4	187	1985	164	2.41	6.76×10^{-6}	2.0

[a] The measurement was made by the DSC method, described by Kamide and Fujii.[16] Polymer blend (3 mg) was melted under nitrogen at 230°C for 5 min; the polymer melt was cooled to crystallization temperature at a rate of 80°C/min.

[b] Abrami's equation: $\theta = \exp(-k \cdot t^n)$; θ - - -, the fraction of uncrystallized material remaining after t min.

butylperoxy)hexyne-3, which effected the reaction of s-PB with long chain length for vinyl loss and crosslinking.[11] The stabilized s-PB with BZO-X can be press-molded into sheets at 210°C, even in the presence of 2,5-dimethyl-2,5-bis(t-butylperoxy)-hexyne-3, although the sheets were highly crosslinked. The blend of s-PB with peroxide cannot be press-molded without the stabilizer. It is considered that the radical species formed in the initial stage of heating were caught by BZO-X, and after the stabilizers had diminished the crosslinking and vinyl loss occurred in the reaction of radical species.

Melt Spinning of Syndiotactic 1,2-Polybutadiene

A melt-spinning temperature of more than 230°C cannot be applied because of the absence of an effective stabilizer. The polymers used hereinafter contain 1.5% BHT and 1% BZO-H. Occasional breakage of the fibers occurred during melt spinning at 230°C of s-PB with a mp of 195°C. A spinning temperature below 220°C is favorable. Table II shows the relationships between the molecular structure and mechanical properties of the drawn fibers, melt-spun at 205°C and drawn to the nearly maximal draw ratio at 50°C. Fine filaments of about 1 denier were obtained from s-PB with a mp of 145–195°C and MW 20,000–70,000. Higher molecular weight polymer blended with an equal amount of tetralin (Table II, No. 9) were melt-spun in a similar way. The tensile strength was not so high. Higher tenacity fibers were obtained by spinning at low draft and drawing at high stretching ratio, although the diameter was larger than 20 μm. Tenacity of more than 5.5 t/cm^2 could not be found in the s-PB fibers. The modulus is low, especially among s-PB fibers with a mp lower than 170°C. S-PB with a mp of about 185°C is preferable on the basis of spinnability and fiber processability.

The absolute values of birefringence of drawn fibers of s-PB are larger the higher the vinyl content. The higher the melting point of s-PB, the higher the vinyl content. The large positive polarizabilities due to cis-1,4-units oriented
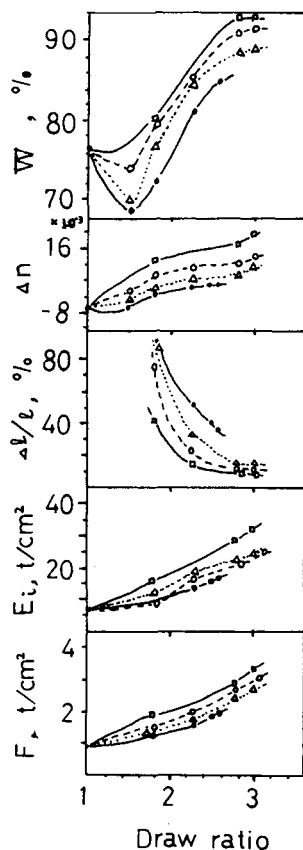
Fig. 4. Mechanical properties and orientation versus draw ratio and drawing temperature (undrawn fiber, No. 5 in Table III); (—□—) 150°C, (- - - O - - -) 100°C, (- - - △ - - -) 60°C, (— ● —) 23°C.

along the fiber axis in a maximally stretched state decreased the absolute value. Kato et al. found the absolute values of birefringence in a released state of uni-axially stretched films of low crystalline s-PB larger than those in a stretched
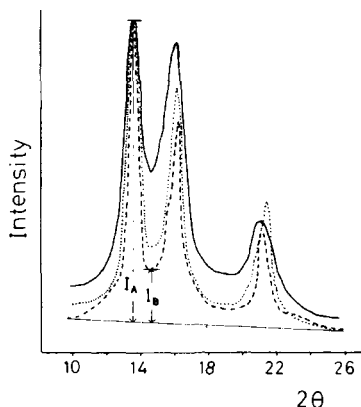

Fig. 5. X-ray spectra of s-1,2-polybutadiene fibers: (- - - -) as-spun fibers; (———) drawn 2.8 at 90°C; (.......) heat set at 150°C for 30 min of drawn fibers.

TABLE V

Influence of Heat-set on the Mechanical Properties and the Structural Parameter of Syndiotactic 1,2-Polybutadiene Fibers[a]

Heat-set temperature (°C)	Structural parameter							Mechanical properties			
	I_B/I_A	B(010)	2θ(210)	B(210)	W (%)	Δn ($\times 10^{-3}$)	density (g/cm³)	D (μ)	F (t/cm^2)	E (t/cm^2)	$\Delta l/1$ (%)
As-Spun fibers	0.17	0.60	21.15	0.55	72.7	−5.7	0.9263	22	0.7	7	267
Drawn fibers (280%) 120	0.45	1.24	20.9	1.44	87.2	−12.5	0.9206	14	1.9	16	16.0
150	—	1.15	21.15	1.08	87.4	−13.6	0.9262	13.7	2.0	13.3	15.3
150	0.22	0.75	21.3	0.95	88.8	−15.0	0.9278	13.7	2.1	12.6	17.8
170	—	—	—	—	—	−15.2	0.9302	13.0	2.1	12.0	18.1
185	—	—	—	—	—	−15.8	0.9410	12.7	1.7	10.0	24.8

[a] The s-PB fibers (MP 190°C, ηa 350P) were heat-set for 30 min at constant length.
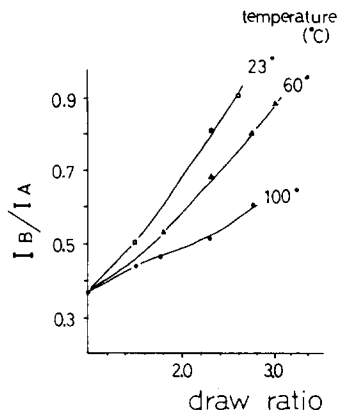
[b] B = half width of plane.

Fig. 6. Ratio of I_B/I_A versus draw ratio and drawing temperature (undrawn fiber, No. 5 in Table III).

state.[12] They concluded that the conformation of the structural unit in an amorphous phase changes from a perpendicular to a parallel structure[13] during stretching.   However, their data can be explained without the conformational change on the assumption that the absolute value of birefringence is not decreased by the contribution of cis-1,4-units in the released state, where the degree of the orientation of cis-1,4-units along the fiber axis is lower than that in a stretched state.

Table III shows the mechanical properties and orientations of the undrawn s-PB fibers with different molecular weights and melting points.   The fibers were melt-spun by the melt-spinning apparatus with a 20-mm extruder at 205°C.   The tenacity and orientation depend on the melt viscosities of the polymer and are almost independent of melting point.   The initial modulus is dependent on melt viscosity and melting point.   The orientation is high even in low molecular weight polymer.   This is attributed to the high spinning draft and rapid rate of crystallization, which is shown in Table IV.   The rate is considered to be further accelerated during melt spinning.[14,15]

The amorphous and/or low orientated fibers with less than 5 denier could not be obtained under any spinning conditions, including the spinning temperature of 220°C, the spinnings into heated cells up to 150°C, and the spinnings into a liquid bath set near the nozzle with a −10°C aqueous salt solution, −60°C methanol, and liquid nitrogen.

Figure 4 shows the drawing behavior of the as-spun fibers No. 5 in Table III versus temperature and draw ratio.   As draw ratio increased, the initial modulus, the tenacity, and the orientation increased.   The ratio of I_B/I_A (Fig. 5) shows the degrees of disorder in the s-PB fibers; the ratio increases with decreasing crystallinity and with decreasing size and increasing degree of distortion of
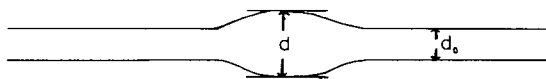

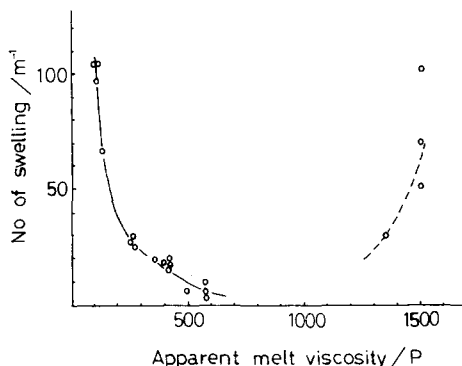Fig. 7. Typical swelling in s-PB fibers.

Fig. 8. Number of swellings versus melt viscosity (spinning apparatus (B), the data for drawn 1-denier fibers).

crystallite. The ratio of I_B/I_A increased with an increase in draw ratio and a lower drawing temperature (Fig. 6). The ratio decreased by heat-set, shown in Table V. When the fibers reacted with $AlBr_3$ in benzene, the rate of cyclization and crosslinking became larger as the ratio of I_B/I_A increased, possibly because of the increase in the penetrating rate of the reagent into the fibers. The s-PB fibers contained small swellings (Fig. 7) here and there along the fiber axis. The formation of the swellings occurred nonperiodically during melt spinning. The number of swellings Ns with diameters 1.3 times larger than those of normal fibers was counted by microscope. The drawn 1-denier fibers with Ns < 0.5/m were obtained from s-PB with mp 170–195°C and ηa 200–800 P by the use of melt-indexer (A). However, the fibers with Ns < 5/m could not be obtained by the spinning apparatus with a 20-mm screw (B). The fibers, melt-spun by the apparatus (B), were cut and melt-spun by (A) and the number of swellings per unit length decreased to the level of the fibers melt-spun directly by (A). More homogeneous mixing can be accomplished by (A), and swellings would have resulted from the inhomogeneity of the melt of s-PB.

The number of swellings Ns by (B) increased for lower molecular weight polymer with ηa < 300 P and for higher molecular weight polymer with ηa > 1200 P (Fig. 8). The spinning apparatus (B) is considered suitable for better mixing the polymer with intermediate melt-viscosity of 300–1200 P. It has been confirmed that the swelling arises by melt spinning of polypropyrene at a lower temperature of 185°C and at high draw-draft and that the swelling of s-PB fibers decreases in melt spinning at low draft. The effect of nonuniform viscosity on the regularity of undrawn fibers was analyzed by Manabe.[18,19] The result of his analysis suggests that the number of swellings increases with the ratio of local viscosities in the regular and irregular part and with spinning draft.

Many different factors can be responsible for irregularity or nonuniformity.[18] In our case this would have resulted from the high draft in melt spinning and the inhomogeneity of the melt of s-PB which was spun at a temperature slightly above the melting point.

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