Preparation of Carbon Fibers from Syndiotactic 1,2-Polybutadiene

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Synopsis

Carbon fibers having good mechanical properties were produced from syndiotactic 1,2-polybutadiene (s-PB). Melt-spun s-PB fibers were made infusible by oxidation, irradiation, or treatments with Lewis acids, protonic acids, or peroxides. The infusibilized fibers were dehydrogenated with oxygen, chloranil, or sulfur and then carbonized. The preparative method by the $AlBr_3$–sulfur–heat treatment process gave carbon fibers with good mechanical strength in a high yield. A filaments bundle was immersed in a benzene solution of $AlBr_3$ (2g/100mL) at 42°C for 78 min under tension, washed with methanol, and then immersed in molten sulfur at 275°C for 14 min. After the adhering sulfur was purged with nitrogen at 290°C for 7 min, the bundle was heated up to a temperature of 700–3000°C under tension in a flow of nitrogen or argon for a few minutes. Carbon fibers heated to 1400°C were obtained with the tensile strength of 16.6 t/cm² and the modulus of 1420 t/cm² in a carbon yield of 82% and strain-graphitized fibers at 3000°C with 20 t/cm² and 4010 t/cm² in 70%.

INTRODUCTION

Carbon fibers have been industrially produced from polyacrylonitrile (PAN) and pitches. PAN gives carbon fibers with excellent mechanical strength in a low carbon yield.[1]

Pitches afford carbon fibers with high modulus and lower strength in a high carbon yield, potentially at a lower cost.[2] A new precursor has been expected, which gives carbon fibers with excellent mechanical properties in a high carbon yield.

Syndiotactic 1,2-polybutadiene (s-PB), which has structural resemblance to PAN, could be a promising raw material for carbon fibers because of the availability at a lower cost, the high carbon content, the melt spinnability and the high reactivity of the polymers.[3,4] The preparation[5] and the melt spinning[6] of s-PB for carbon fibers were described in the previous articles.

A thermally stable powdery polymer was prepared by Kiji and Iwamoto by the aromatization of cyclized 1,2-polybutadiene with chloranil.[7] The carbon fabric, Pluton (Minnesota Mining & Mfg. Co.), was reportedly made from 1,2-polybutadiene[3,8]; however, the production processes have not been made clear by the maker. There have been confusing descriptions in the literature[3,8] concerning the synthetic methods for carbon fibers from polybutadiene.

This paper describes the preparation of carbon fibers from s-PB.

EXPERIMENTAL

Precursor Fibers. The s-PB fibers were prepared by melt spinning at 205°C and stretching in a manner similar to that reported previously.[6] The properties of the fibers used are shown in Table I. These samples consisted of 240 filaments.

Analysis. Infrared spectra were measured by KBr-disk method.[6] Fibers for elemental analysis were dried over P_2O_5 *in vacuo* in a desiccator. The amount of H_2S and CS_2 evolved during heat treatment was determined by FPD–gas chromatography.[5] The amount of H_2S was also determined by the double titration by use of $Cd(CH_3COO)_2$.

Mechanical Properties. Tensile properties of the fibers were measured on an Instron or a similar type of a constant rate of strain testing machine (TOM-5 of Shinko Co. Ltd.) using window technique with 2 cm gauge length and a crosshead speed of 5 mm/min for precursor fibers or 0.2 mm/min for carbon fibers.

Preparation of Carbon Fibers. A preparation through $AlBr_3$–sulfur process was run under tension continuously. The s-PB fibers with 240 filaments at 1.2 den/fil were immersed into 2 wt/vol % solution of $AlBr_3$ in benzene with treating length of 2.4 m and then washed with $HCl–CH_3OH$ (1/20 by weight) and CH_3OH and dried in air. Shrinkage (elongation) can be controlled by changing the supplying speed of fibers on rollers. The typical running speed of fibers on a winding roller is about 3 cm/min.

The way of controlling shrinkage was applied to treatment with sulfur, carbonization up to 1600°C and graphitization up to 3000°C. The $AlBr_3$-treated fibers were immersed into molten sulfur with the treating length of 1 m, and the adhering sulfur of the fibers was purged with nitrogen at 290°C with treating length of 0.3 m. Heat treatment up to 1600°C and also up to 3000°C were carried out under an atmosphere of argon with the treating length of 0.2 m and 0.1 m at maximum temperature, respectively.

Structure Determination. The birefringence of the precursor fibers and the $AlBr_3$-treated fibers was determined with a Nikon polarizing light microscope equipped with a Berek compensator.

Electron microscopy and X-ray diffraction methods were applied to assess a structural feature. The tensile fracture surface of carbon fibers were taken on a scanning electron microscope, HITACHI SSM-2. The transmission micrograph of fragments made by both light grinding and ultrasonic dispersion[9] or cross sections of carbon fibers were obtained on an electron microscope HITACHI HU-12.

The bulk densities were measured in a mixture of bromoform and chloroform using a floating technique.

RESULTS AND DISCUSSION

The preparation of very fine precursor fibers possessing high uniformity and a high degree of molecular orientation is essentially important for the production of high quality carbon fibers. Syndiotactic 1,2-polybutadiene with mp 140–198°C and MW 20,000–70,000 containing stabilizers with 3,5-di-*t*-butyl-4-hydroxybenzyloxy group can be melt-spun at a temperature below 220°C into 1-den fibers to be used for preparation of carbon fibers.[6]
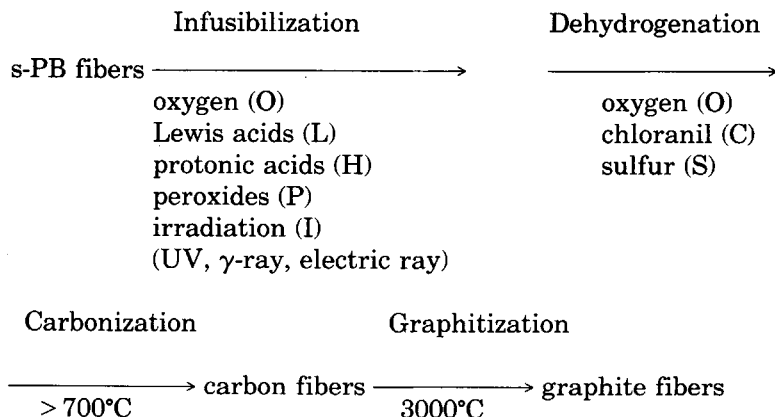
TABLE I
Properties of s-PB Fibers[6]

Experiment	mp (°C)	η_a (p)	Stretching temp ratio	Diameter (μm)	Initial modulus (t/cm²)	Tenacity (t/cm²)	Elongation (%)	No. of swelling (m⁻¹)	Birefringence $\Delta \times 10^3$
24A	187	592	60 × 1.8	14.5	11.4	1.50	68	4	−11.5
25A	185	1350	60 × 2.1	14.4	16.7	2.25	19	15	−12.1
16	192	373	60 × 2.3	14.0	16.9	1.61	18	12	−13.6

The modulus of s-PB fibers with mp lower than 170°C is very low, and s-PB with mp of about 185°C is preferable from the consideration of spinnability and fiber processability. The orientation obtained from the measurement of birefringence and X-ray increases with an increase in a stretch ratio or a temperature of stretching and/or heat set.

The s-PB fibers can be infusibilized by both cyclization and crosslinking by various methods; oxidation, irradiation, or treatments with Lewis acids, protonic acids or peroxides. In the differential thermal analysis of s-PB fibers, the endothermic peak at about 190°C is due to the melting of a crystalline part and the heat of fusion is dependent on a melting point; 15 cal/g for mp 150°C, 18 for 190°C, and 19–22 for 210°C. The exothermic peak at 325°C is due to the thermal crosslinking, and the cyclization of vinyl groups and its enthalpy is independent of an mp and has 300 cal/g. Both the peaks decreased and disappeared with infusibilization. The infusibilized fibers are thermally stable and maintain their shapes in an atmosphere of nitrogen up to 350°C. At about 430°C, they decompose and liquefy.

The infusibilized fibers must be dehydrogenated before carbonization. Dehydrogenation can be accomplished by oxidation or treatment with either sulfur or chloranil. The dehydrogenation must be directed toward the formation of aromatic structures and water, hydrogen sulfide, or tetrachlorohydroquinone (QH_2) and toward avoiding the formation of carbon-containing low molecular compounds except QH_2. The dehydrogenated fibers are black and fireproof. Further aromatization and some carbonization proceed during the heat treatment of the dehydrogenated fibers at 350–450°C and lead to polycyclic aromatics, which show the characteristic peaks at 875, 810, and 750 cm^{-1} in IR spectra.[10]
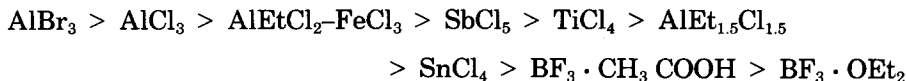
The production processes of carbon fibers from s-PB can be depicted, as shown below.

<pre>
                    Infusibilization   Dehydrogenation

s-PB fibers ──────────────────────→   ──────────────────────→
            oxygen (O)   oxygen (O)
            Lewis acids (L)   chloranil (C)
            protonic acids (H)   sulfur (S)
            peroxides (P)
            irradiation (I)
            (UV, γ-ray, electric ray)

       Carbonization   Graphitization

   ──────────────→ carbon fibers ──────────────→ graphite fibers
       > 700°C   3000°C
</pre>

Various types of manufacturing methods[11] consisting of the combination of infusibilization and dehydrogenation have been compared in order to find a suitable method for the preparation of carbon fibers from s-PB.

The Lewis acid–sulfur process gives carbon fibers with comparably good mechanical properties in a high carbon yield. Lewis acid usable for the process may be, for example, $AlBr_3$, $AlCl_3$, BF_3, $TiCl_4$, $FeCl_3$ and $AlEtCl_2$. The decreasing order of the effect of solvents on the rate of the reaction with $AlBr_3$ is as follows: $CH_2 Cl_2$–benzene–CS_2 > $CH_2 ClCH_2 Cl$ > toluene

$\gg$ nitrobenzene. A cursory investigation of the activity of Lewis acids in benzene gave the following order:

$$AlBr_3 > AlCl_3 > AlEtCl_2\text{--}FeCl_3 > SbCl_5 > TiCl_4 > AlEt_{1.5}Cl_{1.5}$$

$$> SnCl_4 > BF_3 \cdot CH_3 COOH > BF_3 \cdot OEt_2$$

This article describes the results on the preparative method consisting of infusibilization with $AlBr_3$ in benzene, dehydrogenation with sulfur, and heat treatment above 700°C.

Figure 1 shows the decrease of vinyl contents and the increase of both birefringence and weight during the treatment of s-PB fibers with $AlBr_3$. Birefringence changed from -10--16 $\times$ 10^{-3} for the precursor fibers to 10–18 $\times$ 10^{-3} for the $AlBr_3$-treated fibers. The positive polarizability of the $AlBr_3$-treated fibers shows the orientation of the resulting cyclohexane rings along the fiber axis. The structure of fused cyclohexane rings can be depicted as shown in Figure 2 on the assumption of regular trans opening of the double bonds.

The trans opening of the double bonds of s-PB leads to the unstable trans–anti–trans configuration (TAT). The assignment of relative stability, TST > CAC > TAT > CSC, is easily understood on the analogue of perhydroanthracenes (C≡cis, A≡anti, S≡syn). The epimerization of perhydroanthracenes with $AlBr_3$ has been reported by Hill et al.[12] It is considered that unstable-structure TAT is rapidly formed from s-PB with $AlBr_3$, and some of the resulting TAT structure epimerizes gradually by the reaction with $AlBr_3$ to produce more stable form such as CAC or TST.

The fused cyclohexane rings along the fiber axis show large positive birefringence as the calculated data in Table II show. Gaylord et al.[14] regarded the structure of fused cyclohexane rings as a linear ladder type for that from isotactic sequence and as a spiral ladder type for that from syndiotactic sequence.

The X-ray spectra of $AlBr_3$-treated fibers showed an amorphous halo with a peak at $2\theta = 16$; however, the orientation in precursor fibers remained considerable. The values of birefringence increased with decreasing shrinkage during the treatment with $AlBr_3$ (Table III). The larger the birefringence of the $AlBr_3$-treated fibers, the higher the modulus of the resulting carbon fibers.

Table IV shows the intensity of methyl, phenyl, and vinyl groups in IR spectra by changing the concentration of $AlBr_3$ and treating time in the
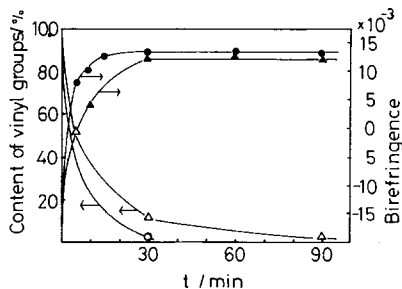

Fig. 1.   Content of vinyl and birefringence vs. $AlBr_3$ treating time. The s-PB fibers were treated with $AlBr_3$ in benzene (2 g/100 mL) at 23°C ($\blacktriangle, \triangle$) and 42°C ($\bullet$, ○).

s-PB   i-PB

↓   ↓

Trans–Anti–Trans   Trans–Syn–Trans
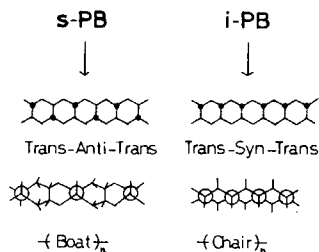

—(Boat)ₙ   —(Chair)ₙ

Fig. 2. Structure of fused cyclohexane rings formed by trans-opening of double bonds of stereoregular 1,2-polybutadiene.

treatment of s-PB fibers with $AlBr_3$. The microstructure of the $AlBr_3$-treated fibers has a complicated composition consisting of fused cyclohexane rings with a step-ladder type, crosslinking, α-phenylethyl groups formed from the Friedel and Craft's reaction of benzene with pendant vinyl groups, isopropenyl groups isomerized from vinyl groups, and so on. The large negative entropy, the large enthalpy, and the easiness of H shift of cationic intermediate products prefer the step-ladder formation to the ladder polymer. A tentative model for the microstructure of the $AlBr_3$-treated fibers is shown below:
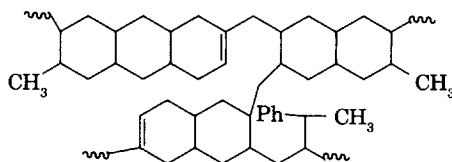

TABLE II
Calculated Birefringence for Fused Cyclohexane Rings[a]

n	Structure	Density (g/mL)	Refractive index			Birefringence ($\Delta n \times 10^3$)
			n_1	n_2	n_3	
1	Cyclohexane	0.7794	1.4350	1.4350	1.3729	31.1
1	Cyclohexene	0.8062	1.4280	1.5030	1.3567	−1.9
2	cis-Decalin	0.898	1.4789	1.4789	1.4561	11.4
2	trans-Decalin	0.872	1.4919	1.4718	1.4022	54.9
3	trans–syn–trans form	0.90	1.5131	1.4826	1.4106	66.5
4		0.90	1.5121	1.4765	1.4052	71.2
5		0.90	1.5114	1.4726	1.4017	74.2
10		0.90	1.5101	1.4643	1.3943	80.8
20		0.90	1.5093	1.4593	1.3904	84.4
50		0.90	1.5089	1.4570 '	1.3879	86.4
100		0.90	1.5047	1.4524	1.3841	86.5
100		0.95	1.5383	1.4818	1.4083	98.3

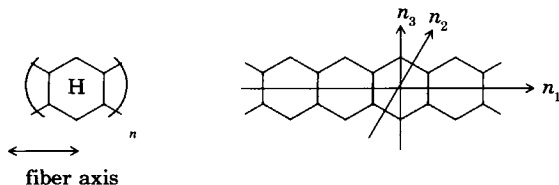[a] The calculation was carried by using the bond polarizabilities given by Le Fevre et al.[13].

fiber axis

TABLE III
Effect of Length on the Birefringence of AlBr$_3$-Treated Fibers[a]

Set	Shrinkage (%) After dryness	Birefringence ($\Delta n \times 10^3$)
0	13.3	13.9
5	17.7	12.3
10	22.4	12.2
20	31	9.4

[a] The s-PB fibers with birefringence of -13.2×10^{-3} were fixed at preset length and were treated with benzene solution of AlBr$_3$ (2 g/100 mL) at 23°C for 6 h and dried free *in vacuo* after washing with methanol.

The rate of infusibilization with AlBr$_3$ in a benzene solution depends not only on the condition of the infusibilization but also on the super molecular structure of the precursor fibers. Figure 3 shows the length of the fibers treated with AlBr$_3$ vs. reaction time as functions of stretching temperatures and heat sets. Figure 4 shows the birefringence of the fibers treated with AlBr$_3$ at 42°C for 30 min vs. the ratio of I_B/I_A.

The ratio of I_B/I_A shows the degree of disorder; I_A is the peak intensity of (010) and I_B is the intensity at $2\theta = 14.5$ in the X-ray spectrum scanned perpendicular to the fiber axis as shown in Figure 5 of the previous paper.[6] The ratio of I_B/I_A increases with decreasing crystallinity, decreasing size, and increasing degree of distortion of crystallite and with lowering temperature of stretching and/or increasing stretch ratio.

The rates of cyclization and crosslinking became larger, possibly because of the increase in the penetration rate of reagents into the fibers as the disorder of s-PB fibers increased. Highly oriented fibers, obtained under high temperature of drawing and/or heat set above 100°C, are not preferable precursors for this production process because of the slow rate of the diffusion of AlBr$_3$ into the fibers.

TABLE IV
Change in Absorbance per Unit Weight (D/ω), during AlBr$_3$ Treatment[a]

Concn of AlBr$_3$ (wt/vol %)	Time (min)	Absorbance per unit weight [$(D/\omega) \cdot$ mg^{-1}] 908 cm^{-1}	1380 cm^{-1}	759 cm^{-1}	697 cm^{-1}
—	—	2.18	—	—	—
2	1	1.63	—	—	—
2	5	1.23	—	—	—
2	30	0.31	0.006	0.011	0.032
2	120	0.065	0.026	0.026	0.044
2	900	—	0.052	0.051	0.073
0.5	30	0.51	0.008	0.020	0.041
1	30	0.24	0.010	0.026	0.049
10	30	0.04	0.046	0.071	0.052

[a] The s-PB fibers were allowed to react by immersing them into benzene solution of AlBr$_3$ at 23°C. The infrared spectra were measured by the KBr-disk methods by using sample weight (ω) in a 200 mg KBr disk. Assignments: 908 cm^{-1} ω (—CH=CH$_2$), 1380 cm^{-1} δ^s(—CH$_3$), 697 cm^{-1} δ_{CH} (monosubstituted benzene), 759 cm^{-1} δ_{CH} (mono- and 1,2-disubstituted benzene).
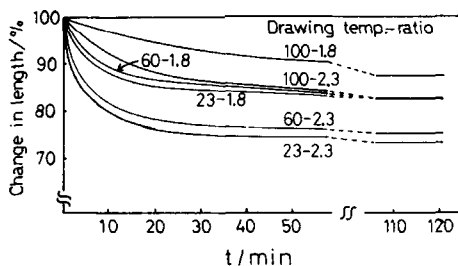
Fig. 3. Influence of drawing condition on the length change during treatment with AlBr₃. The s-PB fibers with mp 189°C were immersed into a benzene solution of AlBr₃ (2 g/100 mL) at 25°C under tension of 30 mg/fil.

Sulfur has been widely used as a dehydrogenizing agent in a carbon industry and for the preparation of aromatic polymers,[15] and the reactions of hydrocarbon with sulfur were reviewed in detail.[16]

The infusibilized fibers were immersed into molten sulfur at 275°C under tension for about 13 min of residence time. The hydrogen/carbon atomic ratio (H/C) of the sulfur-treated fibers was 0.83 (Fig. 5) and the weight was 170% per precursor fibers by the incorporation of sulfur. Hydrogen sulfide evolved during sulfur treatment and succeeding carbonization. Figure 6 shows the amount of H_2S and carbon disulfide eliminated during carbonization. The amount of the carbon disulfide increased with the decrease in H/C of the sulfur-treated fibers.

The stabilized fibers prepared by dehydrogenation with sulfur showed no signs of orientation by X-ray measurement, although the small preferred orientation of glassy carbon was observed in the resulting carbon fibers
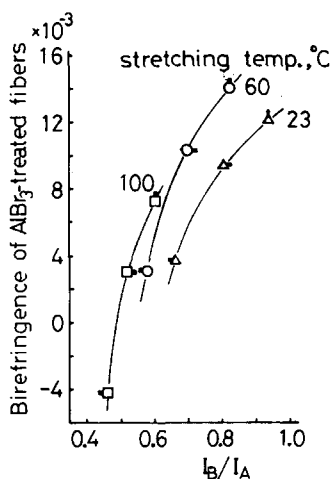

Fig. 4. Change of birefringence of AlBr₃-treated fibers vs. the ratio of I_B to I_A. The s-PB fibers with different values of I_B/I_A were prepared by stretching at different temperatures and draw ratios: (△, ○, □) 1.8; (△ ,○ ,□) 2.3; (△, ○, □) 2.8. The fibers were allowed to react with AlBr₃ in benzene (2 g/100 mL) at 25°C under tension of 30 mg/fil.

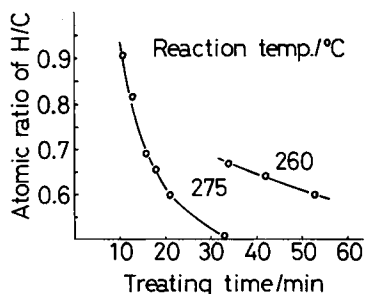Fig. 5. Dehydrogenation of AlBr₃-treated s-PB fibers with sulfur. The s-PB fibers treated with AlBr₃ in benzene (2 g/100 mL) at 42°C for 80 min were dehydrogenated with molten sulfur at 260°C and 275°C.

prepared without tension. This is marked contrast to the stabilized fibers from polyacrylonitrile. In carbon fiber formation from PAN, the essential features of fiber structure, e.g., molecular orientation, are retained.[1] After adhered sulfur was purged with nitrogen at 290°C, the resultant filaments bundle was heated to a temperature of 700–1600°C. The sulfur-treated fibers with H/C of less than 0.65 gave carbon fibers with low mechanical strength.

A heating rate between 400°C and 700°C affected the tensile strength and the sulfur content of carbon fibers (Fig. 7). Tensile strength and sulfur content increased with increase in a heating rate. It was confirmed that tensile strength does not change, but the content of sulfur decreased by heating carbon fibers prepared by heating at the high heating rate of 210°C/min and maintaining at 1000°C for 30 min.

Stretching during carbonization increased the strength and the modulus of resulting carbon fibers (Fig. 8).

Figure 9 shows mechanical properties vs. heating temperature. Tensile strength reached its maximum at 1300–1400°C and began to decrease above 1400°C. A similar decrease of tensile strength has been reported for PAN-based carbon fibers.[17] The tensile strength of carbon fibers is controlled by
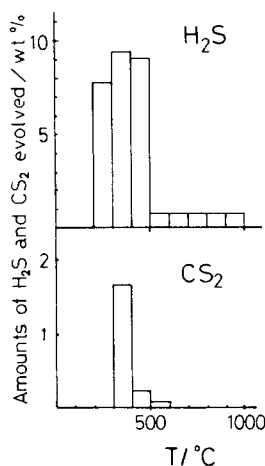

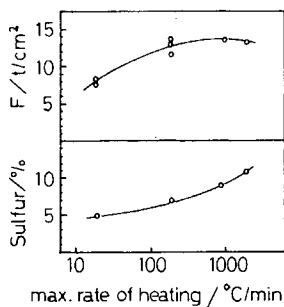Fig. 6. Amounts of H₂S and CS₂ evolved during the carbonization of sulfur-treated fibers per sulfur-treated fibers.

Fig. 7. Influence of heating rate during carbonization to 1000°C on mechanical strength of carbon fibers. The s-PB fibers were infusibilized with AlBr$_3$ in benzene (2 g/100 mL) for 80 min at 42°C and then dehydrogenated with molten sulfur at 275°C for 13 min.
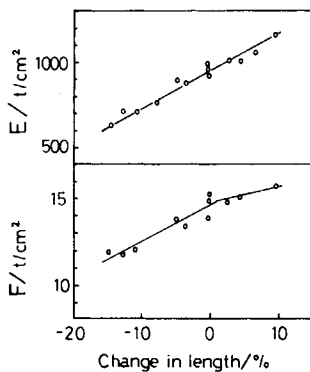

Fig. 8. Influence of stretching during carbonization to 1000°C on the mechanical strength. The stabilized fibers are as in Figure 7.
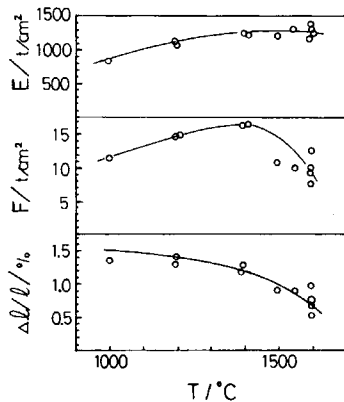

Fig. 9. Mechanical properties of carbon fibers carbonized at different temperatures. The stabilized fibers as in Figure 7.

TABLE V
Effect of Graphitizing Condition on the Mechanical Properties of Graphite Fiber

| | Graphitization | | Graphitized fiber | |
| | Time (s) | Elongation (%) | Tenacity (t/cm²) | Modulus (t/cm²) |
Expt.				
G11	8	10	12.0	2600
G12	40	10	14.7	2780
G13	80	10	17.7	3310
G21	40	10	16.5	2560
G22	40	15	18.4	3480
G23	40	20	20.0	4010
G24	40	25	19.1	4270

both surface and internal flaws.[18,19] Surface flaws could be removed by suitable surface treatment. Volume flaws seemed to originate from polymer precursor. According to the failure mechanism proposed by Cooper and Mayer,[20] a decrease in strength above 1400°C may be due to an increased shearing inside crystallites causing stress concentration and ultimately to the formation of failure cracks. Meanwhile, Moreton and Watt[21] revealed that the strength of carbon fibers prepared from PAN fibers under clean conditions to avoid contamination of impurity particles continues to increase with increasing a heating temperature.

Table V and Figure 10 show the results on the stretch graphitization of s-PB based carbon fibers. The carbon yield of 70% at 3000°C is very high compared with that of about 35% from polyacrylonitrile. However, the large extention of about 20% was necessary during heat treatment at 3000°C to obtain graphite fibers with the high modulus of 4000 t/cm². The stretch–modulus relationships as shown in Figure 10 are reflected by the modulus of carbon fibers heat treated up to 1400°C. The preparation of stabilized fibers with high orientation seems to be essentially important for the production of high modulus carbon fibers.

The wide angle X-ray diffraction characteristics of s-PB based carbon and graphite fibers are consistent with the turbostratic nature of the graphites. The tensile breakage surface of the 1400°C carbon fibers showed a hackle pattern with a void. The fibrillar structure of the graphite fibers stretched
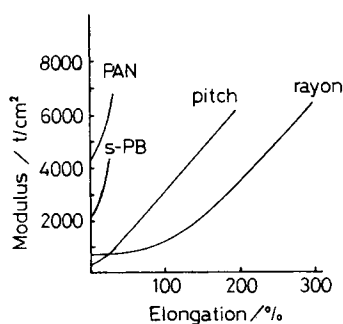
Fig. 10. Stretch–graphitization of carbon fibers from various precursors: Pan—Watt[23]; pitch—Hawthorne[24]; Rayon—Bacon[25], s-PB—this work.

TABLE VI
Typical Operation Condition

Process	Infusibilization			Dehydrogenation		Carbonization	Graphitization
	AlBr₃ treatment	Washing Iª	Washing IIᵇ	Reaction with sulfur	Desulfurization		
Purpose	Cyclization and crosslinking	Removal of AlBr₃	Removal of AlBr₃	Dehydrogenation and aromatization	Removal of adhered sulfur		
Treating	AlBr₃	HCl-MeOH	MeOH	Molten sulfur	N₂	in Ar	in Ar
Temp (°C)	42	25	25	275	270–320	1000–1400	3000
Time (min)	30–80	10	10	11–16	7	3	1
Elongation (%)		−10−−25			0	+5−+10	+20

ª 2 wt/vol AlBr₃/benzene soln.
ᵇ 5 wt/vol HCl/MeOH soln.

TABLE VII
Variation of Fiber

	Elemental analysis (%)				Fiber properties			
	Weight	C	H	S	Diameter (μm)	Elongation (%)	Tenacity (t/cm²)	Modulus (t/cm²)
As-spun fiber	100	88.82	11.18	0	17.1	200	0.98	5.4
Drawn fiber	100	88.82	11.18	0	12.7	23	2.75	20.5
AlBr₃-treated fiber	106	87.34	10.55	0	14.1	20	1.45	23
Sulfur-treated fiber	170	50.34	3.42	46.87	—	10.6	1.30	31
Carbon fiber (1000°C)	93	90.53	0.51	6.73	11.1	1.43	13.6	960
Carbon fiber (1400°C)	82	93.08	0.33	2.75	10.2	1.17	16.6	1420
Graphite fiber (3000°C)	70	100	—	—	8.7	0.50	20	4010

to 15% at 3000°C was affirmed by the electron scanning micrograph of a tensile breakage surface. The transmission micrograph of a cross section or a fragment also showed that composite structure composes of well-developed ribbon sheet and a more tangled and twisted ribbon sheet with the poorly developed lattice structure. The graphite fibers had the specific bulk gravity of 1.77 g/mL and the stacking height of layer planes of 50 Å. Tables VI and VII summarize typical production conditions and the properties of carbon fibers prepared by the AlBr$_3$–sulfur process.

s-PB might be possible to be used for the production of carbon fibers with industrial importance by improving the properties of carbon fibers and the production conditions by reducing flaws and by developing a new process for stabilization, where orientation is kept high.

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