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Effect of a Combination of Drawing and Heat Treatment on the Tensile Properties of Poly[1,3,4-oxadiazole-2,5-diyl-1,4-phenyleneimino(chloroterephthaloyl)imino-1,4-phenylene] Film[1)]

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Poly[1,3,4-oxadiazole-2,5-diyl-1,4-phenyleneimino(chloroterephthaloyl)imino-1,4-phenylene] (PBO-ClT) was prepared by the low-temperature solution polycondensation of 2,5-bis(*p*-aminophenyl)-1,3,4-oxadiazole with 2-chloroterephthaloyl dichloride in the presence of lithium carbonate as an acid accepter in 1-methyl-2-pyrrolidinone (NMP). The value of the inherent viscosity of PBO-ClT was 1.79 $\mathrm{dl\,g^{-1}}$ in sulfuric acid (0.5 g/100 ml, 25 °C). PBO-ClT was easily dissolved in NMP and *N,N*-dimethylacetamide (DMA). The solubility of PBO-ClT, chloro-substituted polymer, was larger than that of poly(1,3,4-oxadiazole-2,5-diyl-1,4-phenyleneiminoterephthaloylimino-1,4-phenylene) in these organic solvents. In order to enhance the tensile properties of PBO-ClT films cast from NMP solutions, the films were drawn and heat-treated under various conditions. The films were drawn in a DMA/water mixture (80 : 20, v/v, 70 °C) and subsequently heat-treated (the temperature was raised from room temp to 300 °C at a heating rate of 12—15 $\mathrm{°C\,min^{-1}}$). The values of the tensile strength, tensile modulus, and breaking energy of the drawn and heat-treated films were 1.30 GPa, 22.8 GPa, and 37.3 $\mathrm{MJ\,m^{-3}}$, respectively. These values were changed into 1.02 GPa, 18.5 GPa, and 26.9 $\mathrm{MJ\,m^{-3}}$ after 2 h of heat-aging at 350 °C in air. These results showed the high-temperature durability of the drawn and heat-treated materials.

Aromatic polyamides having rigid rod segments have high glass transition temperatures and high melt transition temperatures. These polymers also have good heat-resistant properties. However, they have disadvantages of being difficult to dissolve in organic solvents and difficulty in melt-fabrication. In order to solve these problems, flexible groups, such as –O–, –S–, and –CO–, were introduced into the main chains, and bulky substituent groups were also introduced onto the sides of the main chains,[2)] though the heat-resistant properties of the polymer were slightly deteriorated. Some aromatic polyamides containing chlorophenylene groups in the main chains were soluble in organic solvents, such as 1-methyl-2-pyrrolidinone (NMP), *N,N*-dimethylacetamide (DMA), and hexamethylphosphoric triamide (HMPA); these cast films had good heat-resistant properties.[3,4)]

Preston et al. reported on the syntheses and heat-resistant properties of some aromatic polyamides containing oxadiazole rings in the main chains.[5—12)] They described that poly(1,3,4-oxadiazole-2,5-diyl-1,4-phenyleneiminoterephthaloylimino-1,4-phenylene) [PBO-T; η_{inh} 2.58 $\mathrm{dl\,g^{-1}}$ (0.5 g/100 ml in sulfuric acid, 25 °C)] had good heat-resistant properties and tensile properties (Chart 1): Tensile strength (S) 804 MPa; elongation at break (E) 7.5%; tensile modulus (M) 15.6 GPa.[11)]

PBO-T is soluble in the NMP and DMA containing lithium chloride, but insoluble in NMP, DMA, and HMPA. So, it was very difficult to make these cast films.

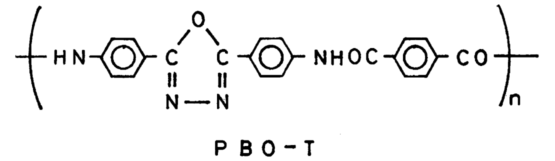
Poly[1, 3, 4-oxadiazole-2, 5-diyl-1, 4-phenyleneimino(chloroterephthaloyl)imino-1,4-phenylene] (PBO-ClT) has not been reported (Chart 2).

The authors reported that aromatic polyamide films having good tensile properties were obtained by methods whereby the films were drawn in organic solvents (swell-drawing) and subsequently heat-treated under tension.[3,4,13—20)]

In this paper we describe the tensile and heat-resistant properties of PBO-ClT films treated by heat-drawing and swell-drawing with a subsequent heat treatment.

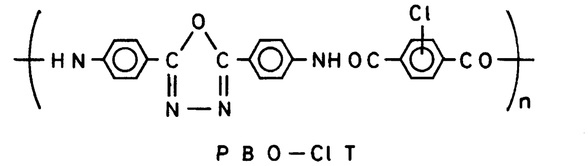
Experimental

Preparation of 2,5-Bis(*p*-aminophenyl)-1,3,4-oxadiazole (BO). *p*-Nitrobenzoyl chloride was prepared from *p*-nitrobenzoic acid with phosphorus pentachloride according to the procedure of Adams and Jenkins: Yield 95.0%; bp 135 °C/1.2 kPa.[21)] *N,N*-bis(*p*-nitrophenyl)hidrazine was prepared from *p*-nitrobenzoyl chloride with hidrazine sul-



PBO-T

Chart 1.



PBO-ClT

Chart 2.

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##Present adress: Yamanashi Prefectural Fuji Industry Technology Center, 205, Shimoyoshida, Fujiyoshida 403.

fate: Yield 80.3%.[22] This hydrazine was converted into 2,5-bis(*p*-nitrophenyl)-1,3,4-oxadiazole with phosphoryl chloride according to the procedure of Preston: Yield 90.8%.[22] BO was prepared by reduction of 2,5-bis(*p*-nitrophenyl)-1,3,4-oxadiazole with sodium disulfide in pyridine and purified by recrystallization from 2-metoxyethanol/water (9:10, v/v): Yield 80.4%; MS (70 eV) m/z (rel intensity) 252 (M^+; 100). Anal. Calcd for $C_{14}H_{12}N_4O$: C, 66.66; H, 4.79; N, 22.21%. Found: C, 67.34; H, 4.59; N, 22.47%.[23,24]

Preparation of 2-Chloroterephthaloyl Dichloride (ClT). 2-Chloroterephthalic acid was prepared by the oxidation of 2-chloro-*p*-xylene with alkaline potassium permanganate according to the process described by Smith: Yield 80.8%.[25] ClT was prepared by the chlorination of 2-chloroterephthalic acid with phosphorus pentachloride and purified by distillation: Yield 83.0%; bp 124 °C/0.4 kPa.

Preparation of PBO-ClT. NMP was purified by vacuum distillation over calcium hydride: Bp 50—51 °C/0.40 kPa. PBO-ClT was prepared by low-temperature solution polycondensation of BO with ClT in the presence of lithium carbonate as acid accepter in NMP (Chart 3). To a solution of 4.036 g (0.016 mol) of BO in 40 ml of NMP was added 3.800 g (0.016 mol) of ClT at once; the mixture was then stirred at −25 °C for 30 min in a nitrogen atmosphere. After 30 min, to the mixture was added 1.182 g (0.016 mol) of lithium carbonate, as an acid acceptor, and 10 ml of NMP, and was continuously stirred for 3 h. During this period, a highly viscous solution which was difficult to stir was obtained. 50 ml of NMP was added to the solution in five approximately equal portions to attain efficient stirring. The viscous polymer solution was poured into distilled water, with rapid stirring in a blender. The polymer was collected on a sintered-glass filter, and washed three times in the blender with water and finally with ethanol. The PBO-ClT was dried over night at 70 °C in a vacuum oven: Yield 6.40 g (96.0%); IR 3300, 1650 (amide) and 1600, 1500, 845 cm^{-1} (benzene ring). Anal. Calcd for $C_{22}H_{13}ClN_4O_3$: C, 63.39; H, 3.14; N, 13.44%. Found: C, 62.52; H, 3.37; N, 12.97%.

Preparation of PBO-ClT Films. Twenty ml of NMP, 0.25 g of PBO-ClT, and a teflon-covered stirring bar were placed in a 50 ml stoppered flask and the mixture was magnetically stirred. This solution was then cast onto a glass plate (about 100 cm^2) and dried at 80 °C, for 48 h. The films were washed with ethanol in order to remove any residual NMP in the films, and then dried at 50 °C, for 5 h, in a vacuum oven. Films with a thickness of 40—50 µm were obtained.

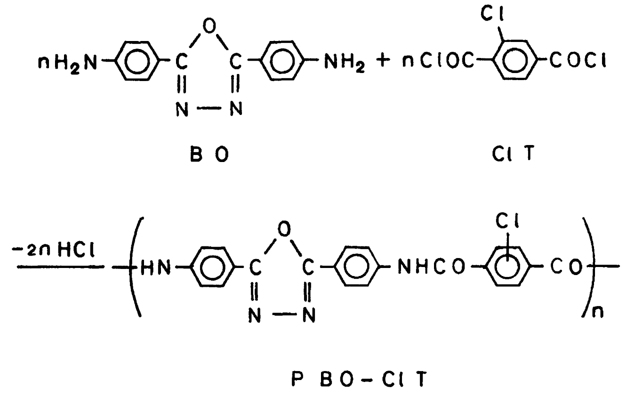

Chart 3.

Measurements. Thermogravimetric-differential thermal analysis (TG-DTA) was performed with Rigaku TG-DTA Model 8112H on a roughly 8 mg sample at a heating rate of 10 °C min^{-1} in a stream of nitrogen.

The weight of the organic solvent that the films absorbed during immersion (weight gain) was calculated using

$$\text{Weight gain } (\%) = 100(w_b - W_a)/W_a,$$

where W_a is the weight of the films before immersion in an organic solvent, and w_b is their weight after immersion.

The tensile properties were measured on a Toyo Baldwin Tensilon UTM-II at a strain rate of 10 mm min^{-1} at 20 °C and 60% RH. Measurements were performed with untreated and treated film specimens (20 mm of gauge length, 1—2 mm wide, 20—50 µm thick). The values of the breaking energy were calculated from the stress-strain curves.[26]

Results and Discussion

The value of the inherent viscosity of PBO-ClT was 1.79 dl g^{-1} in sulfuric acid (0.5 g/100 ml, at 25 °C).

The TG-DTA curves of PBO-ClT are shown in Fig. 1. The DTA curve shows the endothermic peak due to the melt transition and the heat-decomposition at 503—578 °C (top of peak: 531 °C), the small exothermic peak due to crystallization at 300 °C, and the small change due to glass transition at 236 °C. Preston et al. reported that the melttransition temperature of PBO-T was 515 °C.[11]

The TGA curve shows a rapid weight loss at 450 °C; about a 50% weight loss had occurred by the time that the temp. reached 800 °C. This polymer suggested a considerable heat-resistant property.

The solubilities of PBO-ClT and PBO-T are shown in Table 1. PBO-ClT was easily dissolved in NMP and DMA without containing lithium chloride. It was found that the solubility of PBO-ClT, a chloro-substituted polymer, was larger than that of PBO-T in NMP, DMA, or HMPA.

Clear and tough films (**1** in Table 2) were obtained from an NMP solution of PBO-ClT. Table 2 shows

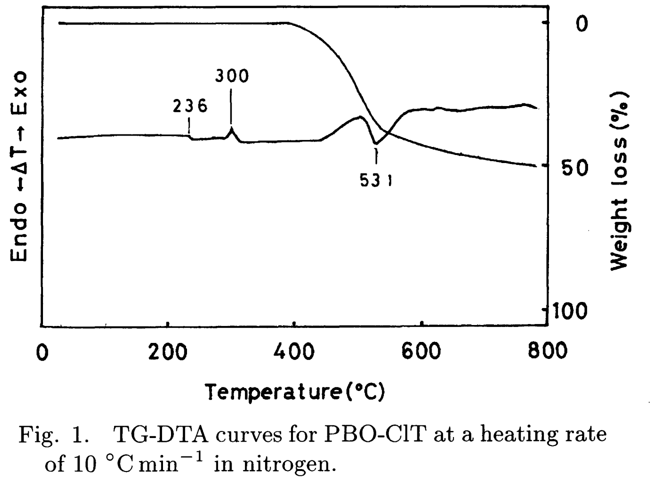

Fig. 1. TG-DTA curves for PBO-ClT at a heating rate of 10 °C min^{-1} in nitrogen.

Table 1. Solubility of PBO-ClT and PBO-T[a)]

Solvents	PBO-ClT	PBO-T
N,*N*-Dimethylformamide (DMF)	±	−
DMA	++	−
NMP	++	−
HMPA	+	−
DMF/Lithium chloride (95 : 5 by wt)	++	−
DMA/Lithium chloride (95 : 5 by wt)	++	++
NMP/Lithium chloride (95 : 5 by wt)	++	++
HMPA/Lithium chloride (95 : 5 by wt)	++	−

a) ++ denotes soluble at room temperature; + denotes soluble on heating; ± denotes swelling; − denotes insoluble.

the values of the tensile properties that were calculated from the stress–strain curves of films treated under various conditions.

In order to enhance the tensile properties of PBO-ClT films, the films were drawn and heat-treated under various conditions.

The films were heat-drawn at a constant temperature in air with a hand tensile machine after referring to the results of the TG-DTA data. In order to determine the optimum temperature for heat-drawing of the films, the films were drawn at 100—350 °C, and the values of the draw ratio at the break, tensile properties and birefringence (Δn) of the drawn films were measured. These values of films drawn at 250 °C were larger than those of films drawn at other temperatures.

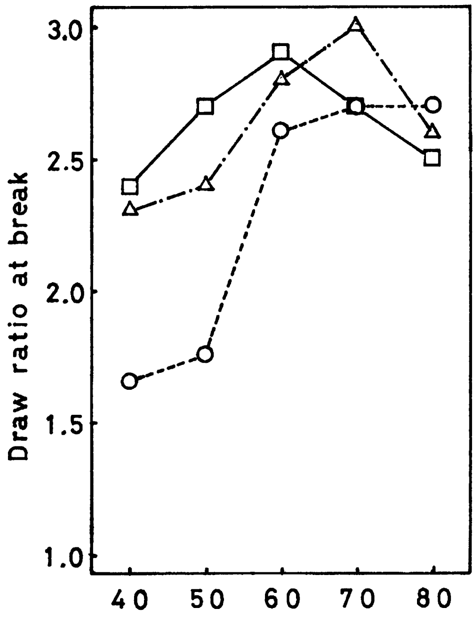

Fig. 2. Dependence of the draw ratio upon breakage on the temperature and composition of a swelling solvent. DMF/water (70 : 30, v/v) (○), DMF/water (80 : 20, v/v) (△), DMF/water (90 : 10, v/v) (□).

The values of Δn and the tensile properties of the 1.8-fold drawn films at 250 °C are given in Table 2 (**2**). The values of S and M of heat-drawn films are about 2.0- and 4.1-times as large as those of undrawn films (**1**). The properties of the heat-drawn films were rigid and slightly brittle; larger values of the tensile properties weren't obtainable by heat drawing.

The authors have reported that aromatic polyamide films having good tensile properties were obtained by the combined method of swell-drawing and subsequent heat-treatment under tension.[3,4,13—20)]

PBO-ClT films were drawn in various organic solvents in order to swell them. In order to determine the optimum conditions for swell-drawing of the films, the

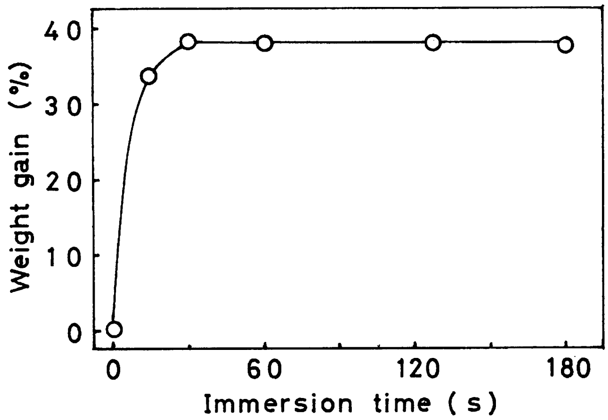

Fig. 3. Changes in the swelling solvent contents of PBO-ClT films with the immersion time.

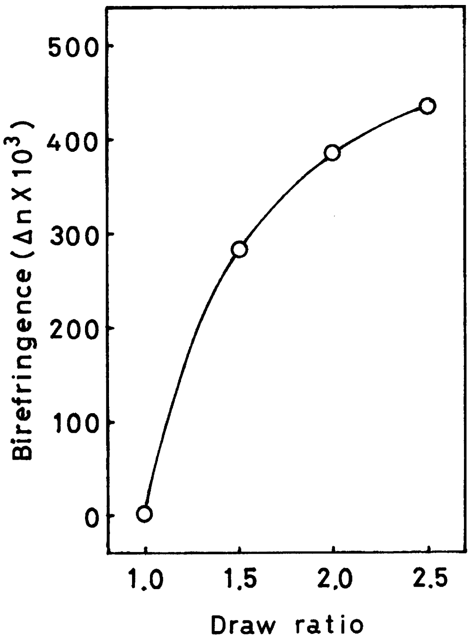

Fig. 4. Relationship between the draw ratio and birefringence for swell-drawn PBO-ClT films.

Table 2. Effect of Combination of Drawing and Heat Treatment on the Tensile Properties of PBO-ClT Films

		Drawing and heat-treatment conditions								
			Temp	Tension		Birefringence	Strength at break	Elongation at break	Tensile modulus	Breaking energy
Sample	DRBT[a]	Methods	°C	MPa	DRAT[b]	×10^3	MPa	%	GPa	$\mathrm{MJ\,m^{-3}}$
1	1.0	Undrawn film				0	247	77.4	2.81	75.3
2[c]	1.0	Heat-drawing	250		1.8	322	488	7.67	11.5	20.3
3[d]	1.0	Swell-drawing	70		2.5	434	660	12.8	10.6	43.2
4[e]	2.5	Heat treatment under tension in nitrogen	300[f]	70	3.4	654	1300	5.97	22.8	37.3

a) DRBT: Draw ratio before treatment. b) DRAT: Draw ratio after treatment. c) Heat-drawing at 250 °C in air. d) Swell-drawing at 70 °C in a DMF/Water (80 : 20, v/v) mixture. e) Heat-treatment of the swell-drawn films (**3**) under tension in nitrogen. f) Temperature was raised from room temp. to 300 °C at heating rate of 12—15 °C $\mathrm{min^{-1}}$, and cooled immediately.

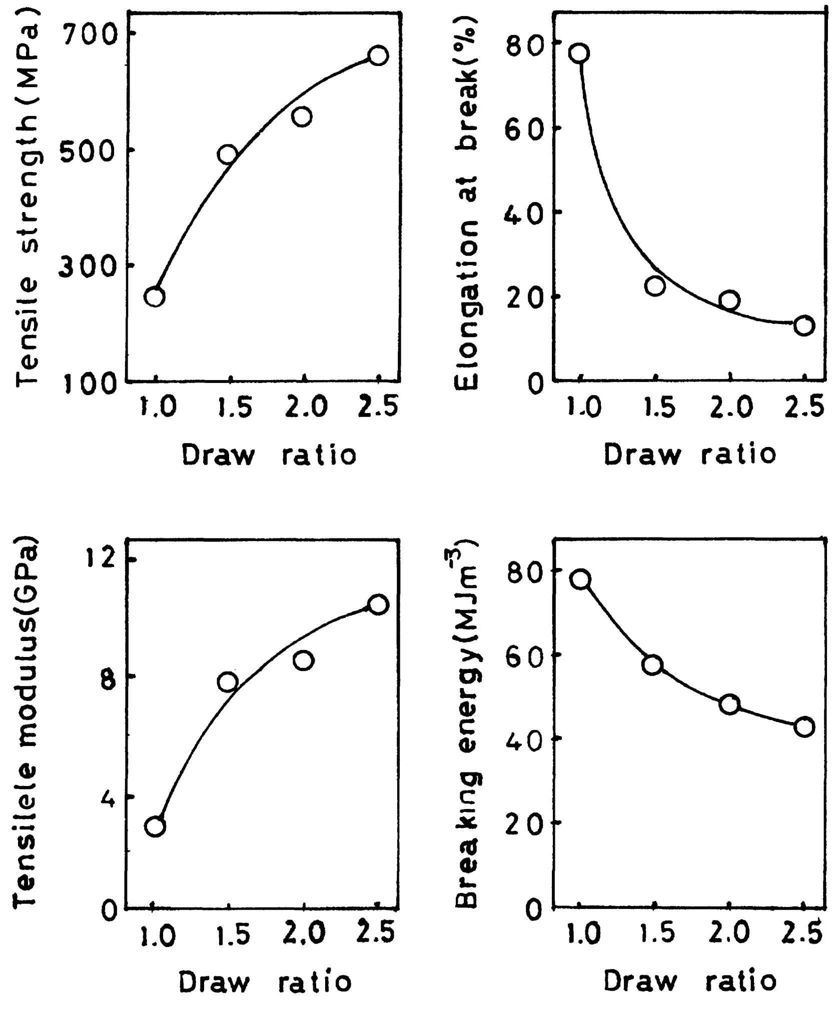

Fig. 5. Relationship between the draw ratio and tensile properties of swell-drawn PBO-ClT films.

values of the draw ratio at the break, and the tensile properties, and Δn of the swell-drawn films under various conditions were measured. These values of swell-drawn films in a DMF/water mixture were larger those of swell-drawn films in other solvents. Figure 2 shows the relationship between the draw ratio at breakage and the temperature in changing the mixture ratio of DMF to water. The value of the draw ratio at breakage of swell-drawn films in a DMF/water (80/20, v/v) mixture at 70 °C was the largest. The values of Δn and the tensile properties of the films were also larger than those of films drawn under other conditions.

Figure 3 shows the relationship between the immersion time in a DMF/water (80 : 20) mixture at 70 °C

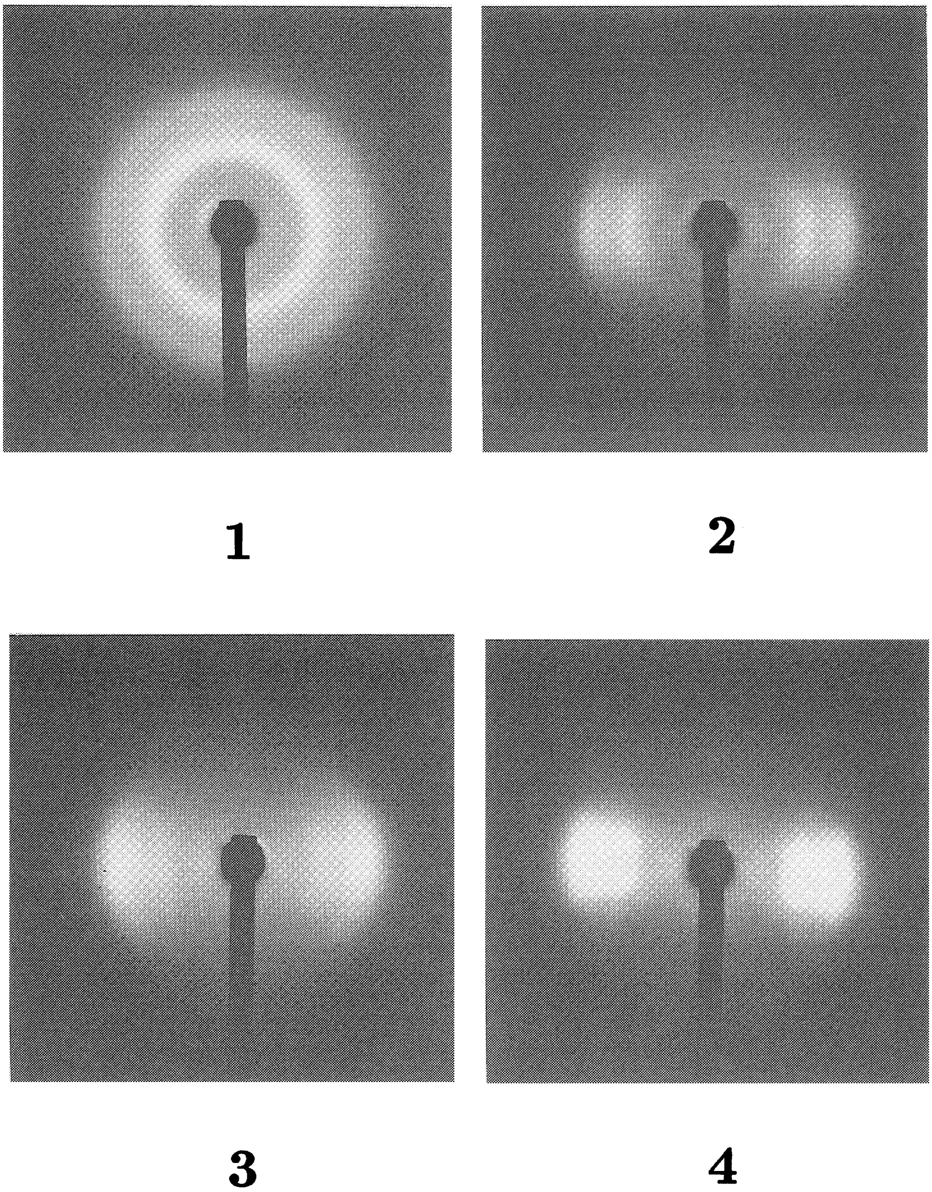

Fig. 6. X-Ray diffraction patterns of samples **1**, **2**, **3**, and **4**.

and the weight gain of the films. The weight gain of the films approached a constant value (38%) 30 s after the films were immersed in the solution. The films were drawn after 3 min in order to ensure that they had gained maximum weight.

Figures 4 and 5 show a change in the values of Δn and the tensile properties of swell-drawn films along with an increase in the draw ratio, as described above, in the best case. Although the values of Δn, S, and M increased along with an increase in the draw ratio, the value of E and the breaking energy (B) decreased along with an increase in the draw ratio. Generally, the values of the breaking energy are greatly affected by the values of elongation at breakage.

The values of Δn and the tensile properties of the 2.5-fold swell-drawn films at 70 °C are shown in Table 2 (**3**). In spite of the high glass-transition temperature of PBO-ClT, the swell-drawing enhanced the tensile properties of the films at near to room temperature.

The values of S, E, M, and B of 2.5-fold swell-drawn films are compared with those of 1.8-fold heat-drawn films: M; Heat-drawn$\geqq$Swell-drawn. T, E, and B; Swell-drawn$>$Heat-drawn. These results suggest that 2.5-fold swell-drawn films are more flexible and tougher than those of heat-drawn films. The difference between the properties of swell-drawn films and that of heat-drawn films arose from the different methods of drawing. Swell-drawing was carried out in an organic solvent at a low temperature, and the orientation of the molecular chains of the films was enhanced. However, the increase in the crystallinity of the films was less than that of heat-drawn films at high temperature.[27] The

Table 3. Tensile Properties of the Sample **1** and **4** Films after Heat Aging at 350 °C in Air

Sample	Time	Birefringence	Strength at break	Elongation at break	Tensile modules	Breaking energy
	min	$\times 10^3$	MPa	%	GPa	$\mathrm{MJ\,m^{-3}}$
	0	0	247	77.4	2.81	75.3
1[a)]	60	0	179	24.0	3.08	28.2
	120	0	184	21.0	3.49	24.5
	0	654	1300	5.97	22.8	37.3
4[b)]	60	634	1190	5.84	19.1	33.6
	120	606	1020	5.47	18.5	26.9

a) Undrawn films. b) Swell-drawn and subsequently heat-treated films.

flexiblility and toughness of swell-drawn films enhanced the effect of the heat treatment under tension (as described below).

Larger values of the films weren't obtained by only swell-drawing. Therefore, the swell-drawn films were subsequently heat-treated under tension in nitrogen.

The heat-treatment conditions, that is, the rate of heating temperature and the upper temperature limit, were determined by reference to the TG-DTA curves of untreated PBO-ClT as well as the values of Δn and the tensile properties of the heat-treated films. The rate of the heating temperature was 12—15 $^\circ\mathrm{C\,min^{-1}}$ and the upper temperature limit was 300 °C. The value of the tension during a heat treatment was determined as being the maximum value at which films didn't break during the heat treatment; this value was 70 MPa. The values of the birefringence and tensile properties of swell-drawn and subsequently heat-treated films under a tension of 70 MPa at 300 °C are shown in Table 2, sample **4**.

These values were larger than those of the swell-drawn films. The value of birefringence of the film was 654×10^{-3}, and the values of S and M of the heat-treated films were about 5.3- and 8.1-times as large as those of undrawn films. These values were larger than those of PBO-T, as reported by Preston.[11)]

The X-ray diffraction patterns of the undrawn (**1**), heat-drawn (**2**), swell-drawn (**3**), and swell-drawn and subsequently heat-treated film (**4**) are shown in Fig. 6. The value of birefringence and the X-ray diffraction pattern of **4** suggest that the orientation of molecular chains and the increase in the crystallinity of the films were enhanced by the heat treatmet under tension.

The tensile properties of the heat-drawn films to be subsequently heat-treated under tension didn't show large values. The heat-drawn films were broken under high tension during a heat treatment; under low tension, they didn't have good tensile properties. These results were caused by the rigid and brittle property of the heat-drawn films (as described above).

If cleavages of the main chains are brought forth by thermooxidative degradation, and even if the TG-DTA curves do not change, the values of the tensile properties of the films decreased.

Table 3 shows the tensile properties of **1** and **4** after heat aging at 350 °C in air for 60 and 120 min. Although the values of S and M of **4** were changed into 1.02 and 26.9 GPa after 2 h of heat aging at 350 °C in air, these values of S and M were 4.1- and 6.6-times as large as those of untreated films (**1** in Table 2). These results showed the high-temperature durability of the swell-drawn and subsequently heat-treated materials.

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