

## 폴리이미드 섬유의 합성과 그 특성

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## Synthesis and Characterization of Polyimide Fibers

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**요 약 :** p-Chlorophenol 용제를 사용하여 1단계 방법으로 3,3'-dimethyl-4,4'-diaminobiphenyl (OTOL)와 3,3',4,4'-biphenyltetra-carboxylic dianhydride (BPDA), 그리고 두 단량체, 4,4'-diaminodiphenyl ether (ODA)와 2,2'-bis(trifluoromethyl)-4,4'-diaminobiphenyl (PFMB)를 사용하여, p-chlorophenol에 녹는 여러가지 공중합체를 만들었다. 첫번째 단량체로 만든 공중합체의 점도는 4.35~5.43 dL/g였다. 이 공중합체 용액을 방사하여 섬유를 만들었으며 이들의 인장강도는 7.67~16.28 g/d였다. 두번째 단량체를 만든 공중합체의 점도는 3.48~6.98 dL/g였고, 이 공중합체 용액을 방사하여 만든 섬유의 최고 인장강도는 15.10 g/d, 최대 탄성율의 값은 810 g/d였다.

**Abstract :** The random copolymerization of 3,3'-dimethyl-4,4'-diaminobiphenyl (OTOL) and 3,3',4,4'-biphenyltetra-carboxylic dianhydride (BPDA) with two comonomers, i.e., 4,4'-diaminodiphenyl ether (ODA) and 2,2'-bis(trifluoromethyl)-4,4'-diaminobiphenyl (PFMB), was carried out using the one-step method in p-chlorophenol. Several copolymers were obtained that were soluble in p-chlorophenol. In the first series the copolymers' intrinsic viscosities ranged from 4.35 to 5.43 dL/g. The copolymers were dry-jet wet spun into fibers directly from their polymerization mixtures. The fibers were drawn to higher draw ratios of 4.5 to 6.0. The tensile strengths of the fibers were between 7.67 and 16.28 g/d. The second polymers had intrinsic viscosities of 3.48 to 6.98 dL/g. The draw ratios of fibers were much increased. Fibers of the copolymers displayed tensile strengths as high as 15.10 g/d and moduli as high as 810 g/d.

**Keywords :** polyimide fibers, dry-jet wet, tensile strength, modulus, copolymerization.

## INTRODUCTION

Aromatic polyimides are known for their excellent chemical and solvent resistance and their outstanding thermal stability.<sup>1,2</sup> Because of this unusual combination of properties, they are

widely used in high temperature films, coatings, adhesives, and molded parts. Recently, aromatic polyimides have been under extensive development for composites, thin films, and microelectronics due to their dimensional stability and dielectric properties.<sup>3~7</sup> This unusual combination

of properties, however, makes them essentially impossible to fabricate. Thus, they must be processed in the form of their soluble polyamic acid (PAA) precursors, which are subsequently imidized in situ. This two-step synthesis enabled Du Pont Co.<sup>8</sup> to market the first industrial polyimide film, Kapton<sup>®</sup>, which was prepared from 4,4'-diaminodiphenyl ether (ODA) and pyromellitic dianhydride (PMDA). Irwin et al.<sup>9</sup> were the first to prepare fibers from this polymer. The fibers showed excellent high temperature performance, but the tensile strength and modulus were no more than 6.6 g/d and 77 g/d, respectively. Koton et al.<sup>10,11</sup> synthesized several polyimide fibers by the approach of spinning the solution of a polyamic acid to fibers, followed by drawing at relatively low temperature and then thermal imidization. The fibers had tensile strengths and moduli as high as 13 g/d and 1000 g/d, respectively. Most recently, Jinda et al.<sup>12</sup> made an extensive investigation of several PMDA-based polyimide fibers by the two-step method and reported the fibers with the highest tensile strength of 19.7 g/d and moduli of 1310 g/d. However, the fabrication of fibers by this procedure is complicated by the degree of imidization. The PAA solution is also unstable and must be stored and handled with care.

Farrissey et al.<sup>13,14</sup> prepared a series of soluble copolyimides by one-step method from 3,3', 4,4'-benzophenone tetra-carboxylic dianhydride (BTDA) and mixed toluene diisocyanate (TDA) and 4,4'-diphenylmethane diisocyanate (MDA). The fiber, Polyimide 2080<sup>®</sup>, had tensile strengths and moduli of 2.65 g/d and 70 g/d, respectively. Makino et al.<sup>15</sup> also polymerized 3,3',4,4'-biphenyltetra-carboxylic dianhydride (BPDA) and *o*-dianisidine in hot *p*-chloro-

phenol. The polyimide obtained was spun directly from the polymerization mixture to afford fibers. The fibers had tensile strengths and moduli of only 6.5 g/d and 50 g/d, respectively.

The objective of this research was to prepare soluble polyimides by one-step method for spinning into fibers directly. This work was begun with the polymerization of 3,3'-dimethyl-4,4'-diaminobiphenyl (OTOL) with BPDA. Sasaki et al.<sup>16</sup> made this polymer by melt polymerization with an inherent viscosity of 0.85 dL/g. Kaneda et al.<sup>17</sup> polymerized OTOL with BPDA using the one-step method in phenol. The polymer obtained had an inherent viscosity of 2.74 dL/g. In our hands, however, the polymer with an intrinsic viscosity of 9.29 dL/g was obtained.<sup>18</sup> However, the tensile strength of the fibers was 14.0 g/d, which was similar to the value obtained by the previous workers.<sup>17</sup> This low value may be due to the low draw ratio. The fibers could not be drawn to higher draw ratios because the polymer crystallized rapidly during drawing. Fibers could not be drawn once crystallization took place. Thus, the random copolymerization approach was pursued in this work. Any soluble copolyimides obtained were to be spun into fibers and their properties evaluated.

## EXPERIMENTAL

**Materials.** The dianhydride, 3,3',4,4'-biphenyltetra-carboxylic dianhydride (BPDA) was obtained from the Chriskev Corporation. The BPDA was heated at 190°C under reduced pressure overnight prior to use. The 3,3'-dimethyl-4,4'-diaminobiphenyl (OTOL) was obtained from Aldrich Chemical Company. The OTOL was recrystallized twice from ethanol

after neutralization with sodium hydroxide. The 4,4'-diaminodiphenyl ether (ODA) was sublimed under reduced pressure prior to use. The

2,2'-bis(trifluoromethyl)-4,4'-diaminobiphenyl (PFMB) was prepared by the same procedure<sup>19</sup> and was purified by recrystallization from a 1:1 (v/v) mixture of  $\text{CHCl}_3$  and hexane and by sublimation. The p-chlorophenol was obtained from Aldrich Chemical Company and distilled under reduced pressure prior to use.

**Instrumentation.** Intrinsic viscosities were determined with Cannon-Ubbelohde No. 150 and 200 viscometers. Flow times were recorded for p-chlorophenol solutions with polymer concentrations of approximately 0.5 g/dL at  $60 \pm 0.1^\circ\text{C}$ . Differential scanning calorimetry (DSC) analyses were performed in nitrogen with a heating rate of  $20^\circ\text{C}/\text{min}$  using a Du Pont Model 9900 thermal analyzer equipped with a differential scanning calorimetry cell. Thermogravimetric analysis (TGA) analyses were obtained in nitrogen and in air with a Du Pont Model 951 thermogravimetric analyzer with a heating rate of  $10^\circ\text{C}/\text{min}$ . Thermal mechanical analysis (TMA) analyses were performed in nitrogen using a heating rate of  $10^\circ\text{C}/\text{min}$  and a stress of 1MPa with a Du Pont Model 2940 thermal mechanical analyzer equipped with a thermal mechanical probe. Mechanical properties were determined in air using a strain rate of  $8 \times 10^{-4} \text{ s}^{-1}$  and a 22mm long drawn fiber at  $25^\circ\text{C}$  on a Rheometrics solid state analyzer RSA II.

### Polymerizations.

**Typical Copolymerization of OTOL, ODA and BPDA:** A four-necked, 50 mL, resin kettle equipped with an overhead stirrer and a nitrogen inlet was purged with dry nitrogen and

charged with OTOL (0.8000 g, 3.768 mmol), ODA (0.1886 g, 0.9421 mmol) and p-chlorophenol (24 mL). After the solids had dissolved completely, BPAD (1.3859 g, 4.7105 mmol) was added. The mixture was stirred 3h at  $45^\circ\text{C}$ , and then heated gradually to  $207^\circ\text{C}$ . Isoquinoline (10 drops) was added at  $190^\circ\text{C}$ . The mixture was stirred and heated at  $207^\circ\text{C}$  under nitrogen for 12h. The water liberated by the polycondensation was removed by distillation. A portion of the solution was used for fiber spinning. The remainder was diluted with p-chlorophenol (30 mL) and then poured into 700 mL of methanol with stirring. The precipitate that formed was collected by filtration, washed with methanol and agitated in methanol in a blender. The polyimide was collected by filtration and dried under reduced pressure at  $90^\circ\text{C}$  for 24h.

**Typical Copolymerization of OTOL, PFMB and BPDA:** To a 50 mL, four-necked, resin kettle equipped with an overhead stirrer and a nitrogen inlet were added OTOL (0.1000 g, 4.7105mmol), PFMB (0.3771 g, 1.178 mmol) and p-chlorophenol (31.6 mL). After the solids had dissolved completely, BPDA (1.7324 g, 5.881 mmol) was added. The reaction mixture was stirred for 3h at  $60^\circ\text{C}$  and then heated gradually under nitrogen to  $210^\circ\text{C}$ . Isoquinoline (10 drops) was added at  $180^\circ\text{C}$ . The mixture was stirred and heated at  $210^\circ\text{C}$  under nitrogen for an additional 12h. The water liberated by the polycondensation was removed by distillation. A portion of the solution was used for fiber spinning. The copolyimide was separated in the same way as in the above case.

**Fiber Spinning and Drawing Processes.** Polyimide fibers were spun from isotropic p-



## RESULTS AND DISCUSSION

The copolymers **4a-d** displayed good thermal and thermo-oxidative stabilities (Table 2). Their TGA thermograms, which were obtained with a heating rate of 10 °C/min, showed 5 % weight

**Table 1.** Copolymerization of OTOL and ODA with BPDA

Copoly-imide	Molar Ratio of Monomers		Monomer Concentration (wt%)	$[\eta]^a$ (dL/g)
	OTOL	ODA		
<b>4a</b>	8	2	7	5.10
<b>4b</b>	6	4	8	5.43
<b>4c</b>	4	6	9	4.78
<b>4d</b>	2	8	10	4.35

<sup>a</sup> Intrinsic viscosity determined in p-chlorophenol at 60 °C.

**Table 2.** Thermal Properties of OTOL/ODA/BPDA Copolyimides

Copoly-imide	Molar Ratio of Monomers		TGA <sup>a</sup>		TMA	
	OTOL	ODA	N <sub>2</sub>	Air	$T_g^{b,d}$	CTE <sup>c</sup>
<b>4a</b>	8	2	565	465	280	1.6
<b>4b</b>	6	4	567	460	279	3.0
<b>4c</b>	4	6	568	528	277	3.6
<b>4d</b>	2	8	572	561	276	4.2

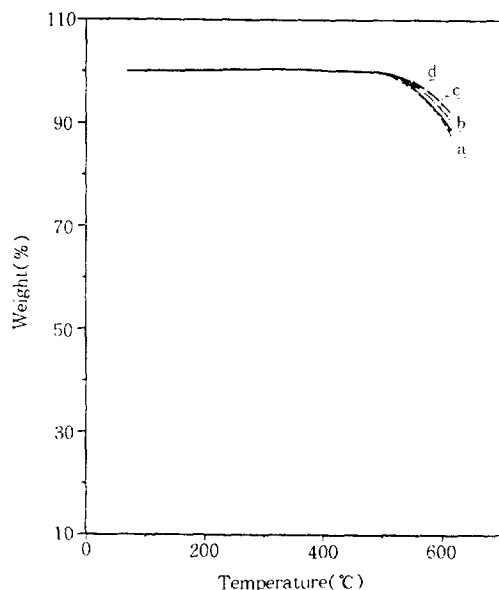
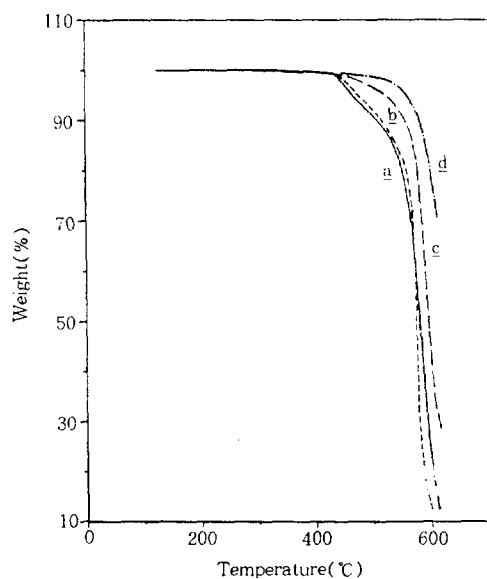
<sup>a</sup> Temperature at which 5% weight loss occurred with a heating rate of 10 °C/min.

<sup>b</sup> Temperature at which a change in slope of the fiber dimensional change versus temperature occurred with a heating rate of 10 °C/min and a stress of 1MPa.

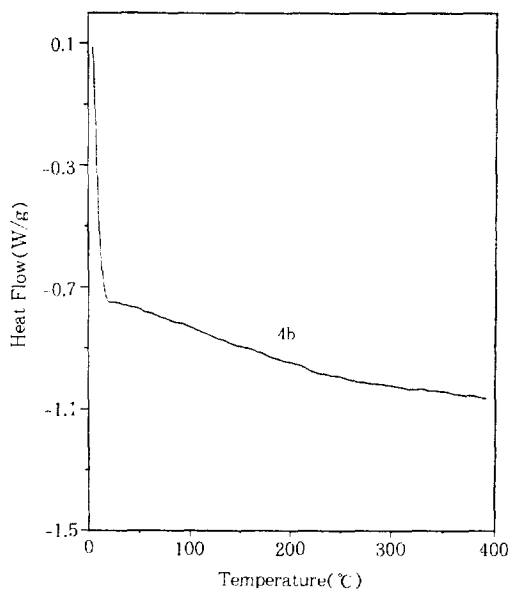
<sup>c</sup> Coefficient of thermal expansion( $\times 10^{-5} \text{ } ^\circ\text{C}^{-1}$ ). The CTE values were determined as the mean between 50 and 200 °C

<sup>d</sup> Could not be detected with DSC.

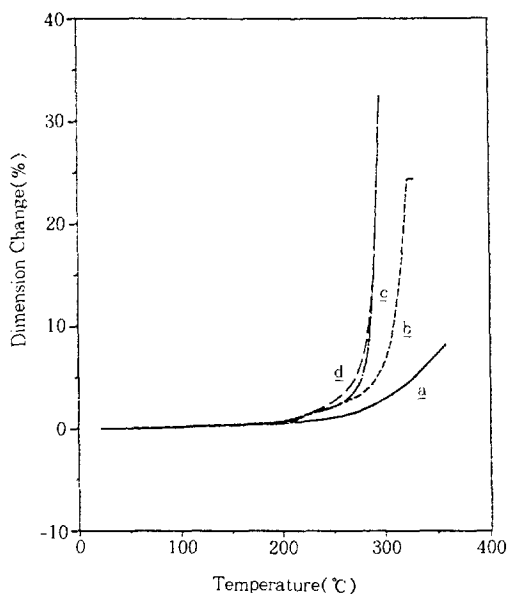
losses in nitrogen between 565 and 572 °C and in air between 465 and 561 °C (Figs. 1 and 2). As shown in Table 2, the copolymers' thermal and thermo-oxidative stabilities increased as their ODA (**2**) content increased. The  $T_g$ s of the copolyimides were impossible to detect with DSC (Fig. 3). Thus, TMA of as-spun fibers was used to determine their  $T_g$ s and their CTEs. In order to eliminate any stress that may have been incorporated in the fibers during processing, the as-spun fibers were annealed at 200 °C for 24h under reduced pressure. The fibers' TMA thermograms, which were obtained with a heating rate of 10 °C/min and an applied stress of 1 Mpa, showed changes in slope in nitrogen between 276 °C and 280 °C (Fig. 4). The


**Fig. 1.** TGA thermograms of copolyimides **4a-d** obtained in nitrogen with a heating rate of 10 °C/min.

**Fig. 2.** TGA thermograms of copolyimides **4a-d** obtained in air with a heating rate of 10 °C/min.

copolymers'  $T_g$ s decreased as their ODA content increased (Table 2). This can be attributed to the fact that ODA is more flexible than



**Fig. 3.** DSC thermogram of copolyimide **4b** obtained in nitrogen with a heating rate of 20°C/min.



**Fig. 4.** TMA thermograms of copolyimides **4a-d** obtained in nitrogen with a heating rate of 10°C/min and an applied stress of 1 MPa.

OTOL. The CTE values for **4a-d** were between  $1.6 \times 10^{-5}$  and  $4.2 \times 10^{-5} \text{ } ^\circ\text{C}^{-1}$  (Table 2). The CTE

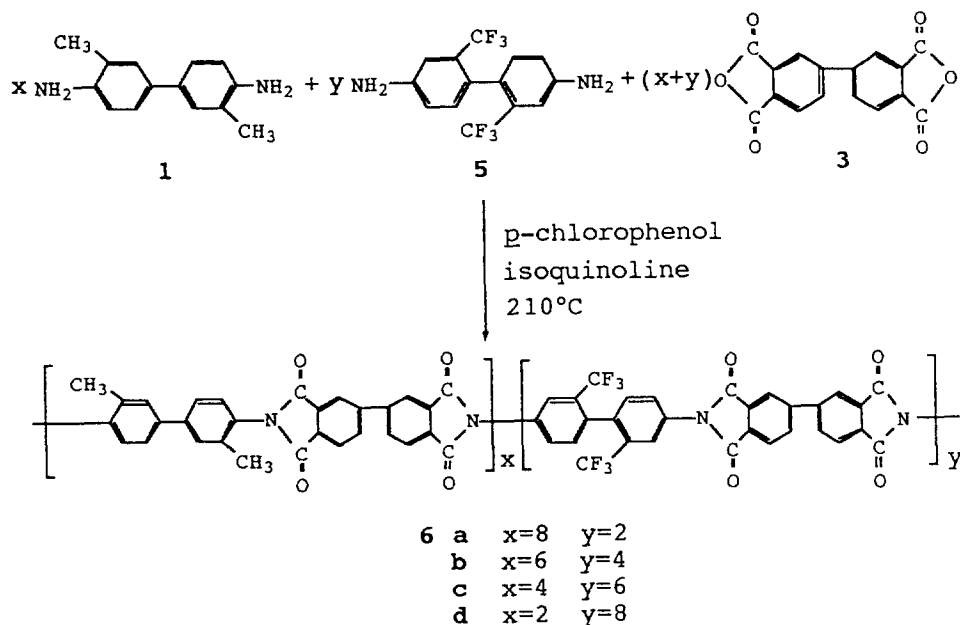
**Table 3.** Preparation and Properties of Fibers of 4

Copolyimide	Dope Temp. (°C)	Drawing Temp. (°C)	Draw ratio	Fibers <sup>a</sup>
				T
<b>4a</b>	60	440	4.5	16.28
<b>4b</b>	90	390	6.0	9.28
<b>4c</b>	90	360	4.5	12.90
<b>4d</b>	90	350	4.5	7.67

<sup>a</sup> T = Tensile strength(g/d).

coefficients increased as the copolymers' ODA content increased. This is further evidence that the incorporation of ODA in the copolymers resulted in more free volume in the matrix.

The copolyimides **4a-d** were spun into fibers directly from their p-chlorophenol polymerization mixtures using a dry-jet wet spinning process (Table 3). The fibers were coagulated in a 1:1 mixture of water and ethanol. The fibers were dried under reduced pressure at 150°C, annealed at 350°C to 440°C, and then drawn to draw ratios of 4.5 to 6.0 (Table 3). Thus, the incorporation of ODA in the OTOL/BPDA system did result in copolymer that could be drawn to higher draw ratios. It appeared that this was because the copolymers' rates of crystallization were slower than that of the homopolymer. This was exactly the effect sought when the regularity of the homopolymer backbone was disrupted through the incorporation of ODA. The tensile strengths of the fibers were between 7.67 g/d and 16.28 g/d (Table 3). The incorporation of 20 mol% of ODA in copolyimide **4a** resulted in fibers that had a higher tensile strength than that of homopolyimide fibers. This can be attributed to their higher draw ratios. However, fibers of the copolyimides that contained higher molar ratios of ODA had lower tensile strengths. Evidently, the positive effect on strength gained by the



Scheme 2

**Table 4.** Copolymerization of OTOL and PFMB with BPDA

Copolyimide	Molar Ratio of Monomers		Monomer Concentration (wt%)	$[\eta]^a$ (dL/g)
	OTOL	PFMB		
<b>6a</b>	8	2	6	5.65
<b>6b</b>	6	4	7	4.27
<b>6c</b>	4	6	9	6.98
<b>6d</b>	2	8	10	3.48

<sup>a</sup> Intrinsic viscosity determined in p-chlorophenol at 60°C.

higher draw ratio was offset by the flexible ether linkage in ODA, which decreased the chain rigidity.

**Copolymerization of OTOL and PFMB with BPDA:** In another attempt to increase the draw ratio of OTOL-based polyimide fibers, copolyimides **6a-d** were prepared according to Scheme 2. The values for x and y shown in Scheme 2 represent the feed ratios of OTOL (**1**) to 2,2'-bis(trifluoromethyl)-4,4'-diaminobiphenyl (PFMB) (**5**) used in the copolymeriza-

**Table 5.** Thermal Properties of OTOL/PFMB/BPDA Copolyimides

Copolyimide	Molar Ratio of Monomers		TGA <sup>a</sup>		TMA	
	OTOL	PFMB	N <sub>2</sub>	Air	$T_g^{b,d}$	CTE <sup>c</sup>
<b>6a</b>	8	2	571	482	280	1.2
<b>6b</b>	6	4	582	511	279	2.1
<b>6c</b>	4	6	596	557	278	2.8
<b>6d</b>	2	8	600	558	275	3.2

<sup>a</sup> Temperature at which 5% weight loss occurred with a heating rate of 10°C/min.

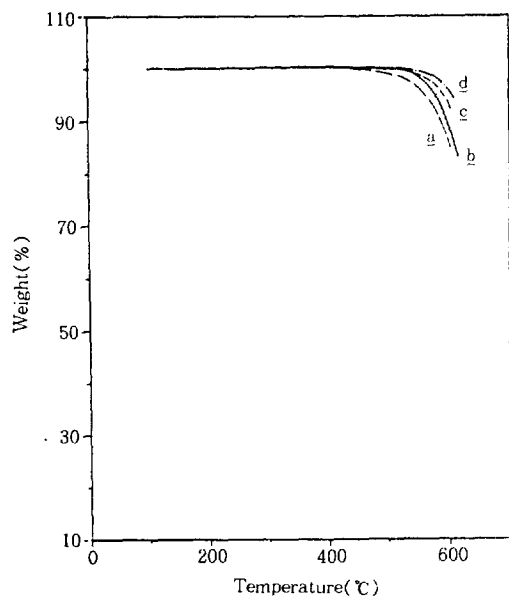
<sup>b</sup> Temperature at which a change in slope of a plot of fiber dimensional change versus temperature occurred with a heating rate of 10°C/min and a stress of 1 MPa.

<sup>c</sup> Coefficient of thermal expansion ( $\times 10^{-5} \text{ } ^\circ\text{C}^{-1}$ ). The CTE values were determined as the mean between 50 and 200°C.

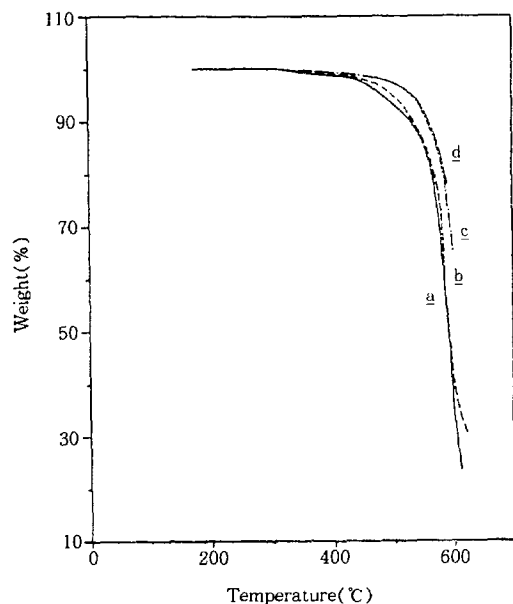
<sup>d</sup> Could not be detected with DSC.

tions. The copolymerizations were carried out with 6~10% (w/w) solids concentrations. The copolymers' intrinsic viscosities in p-chlorophenol at 60°C ranged from 3.48 dL/g to 6.68 dL/g (Table 4).

The copolymers displayed excellent thermal and thermo-oxidative stability (Table 5). Their

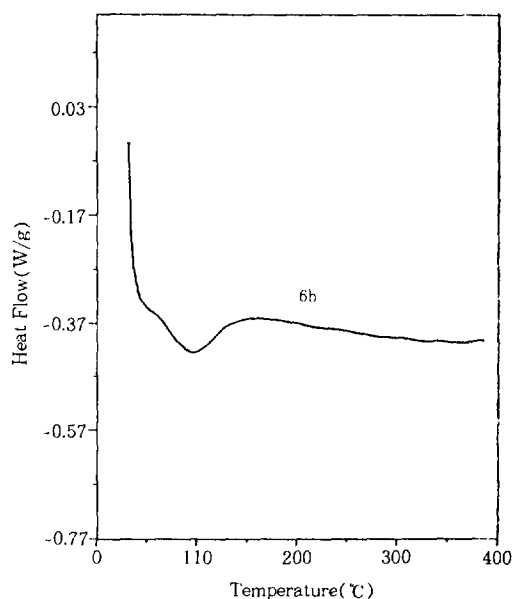


**Fig. 5.** TGA thermograms of copolyimides **6a-b** obtained in nitrogen with a heating rate of 10°C/min.



**Fig. 6.** TGA thermograms of copolyimides **6a-b** obtained in air with a heating rate of 10°C/min.

TGA thermograms, which were obtained with a heating rate of 10°C/min, showed 5% weight losses in nitrogen between 571 and 600°C and



**Fig. 7.** DSC thermogram of copolyimide **6b** obtained in nitrogen with a heating rate of 20°C/min.

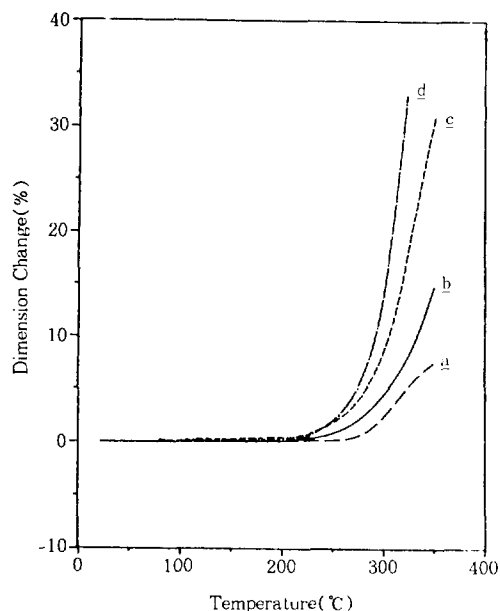
in air between 482 and 558°C (Figs. 5 and 6). As shown in Table 5, their thermal and thermooxidative stabilities increased as their PFMB (**5**) content increased. As with copolyimides **4**, the  $T_g$ s of the copolymers were not observed by DSC (Fig. 7). Thus, TMA of as-spun fibers was used to determine their  $T_g$ s and their CTEs. TMA thermograms showed dramatic changes in slope in nitrogen between 275°C and 280°C (Fig. 8). The copolymers'  $T_g$ s decreased as their PFMB content increased. Since the trifluoromethyl group is larger than the methyl group,<sup>20,21</sup> it can disrupt chain packing more effectively. Thus, copolyimides having higher PFMB (**5**) contents would be expected to have more free volume and, thus, lower  $T_g$ s. The CTE values for **6a-d** were between  $1.2 \times 10^{-5}$  and  $3.2 \times 10^{-5} \text{ } ^\circ\text{C}^{-1}$  (Table 5). The CTE coefficients increased as the copolymers' PFMB content increased. This is further evidence that



**Table 6.** Preparation and Properties of Fibers of 6

Copolyimide	Dope Temp. (°C)	Drawing Temp. (°C)	Draw ratio	Denier	Fibers <sup>a</sup> T/E/M
<b>6a</b>	60	420	4.5	19.0	15.10/2.10/722
<b>6b</b>	60	420	6.0	7.5	10.60/1.84/574
<b>6c</b>	60	420	6.0	5.7	13.46/1.66/810
<b>6d</b>	60	420	6.0	6.8	12.97/2.29/566

<sup>a</sup> T=Tensile strength (g/d); E=Elongation at break(%); M=Modulus(g/d).



**Fig. 8.** TGA thermograms of copolyimides **6a-b** obtained in nitrogen with a heating rate of 10°C/min.

the incorporation of PFMB in the copolymers resulted in more free volume in the matrix.

The copolyimides **6a-d** were spun into fibers directly from their p-chlorophenol polymerization mixtures using a dry-jet wet spinning process (Table 6). The fibers were coagulated in a 1:1 mixture of water and ethanol. The fibers were dried under reduced pressure at 150°C, annealed at 420°C, and then drawn to draw ratios of 4.5 to 6.0 (Table 6). The tensile strengths of the fibers were between 10.60 g/d and 15.10 g/d.

d. The fibers were drawn to higher draw ratios than could be obtained with polyimide of OTOL/BPDA. This resulted in an increase in tensile strength in the case of the fiber prepared from copolyimide **6a**, which contained 20 mol% PFMB. However, copolyimide fibers containing large amounts of PFMB had lower tensile strengths than the fiber of OTOL/BPDA.

## CONCLUSION

The incorporation of 4,4'-diaminodiphenyl ether (ODA) and 2,2'-bis (trifluoromethyl)-4,4'-diaminobiphenyl (PFMB) in the OTOL/BPDA system did result in copolymers that could be drawn to higher draw ratios. The thermal and thermo-oxidative stabilities increased as their ODA and PFMB contents increased. The copolymers'  $T_g$ s decreased as their ODA and PFMB contents increased. This can be attributed to the fact that ODA is more flexible than 3,3'-dimethyl-4,4'-diaminobiphenyl (OTOL). The decrease in  $T_g$ s by increasing the content of PFMB could be due to the disruption of chain packing and, thus, more free volume. The coefficient of thermal expansion (CTE) increased as the copolymers' ODA and PFMB contents increased. The incorporation of 20 mol% of ODA and PFMB in copolyimide resulted in fibers that had a higher tensile strength than that of homopolyimide fibers.

## REFERENCES

1. K. L. Mittal, "Polyimides: Synthesis, Characterization, and Applications," vols. 1&2, Plenum, New York, 1984.
2. M. I. Bessonov, M. M. Koton, V. V.

- Kudryavtsev, and L. A. Laius, "Polyimides : Thermally Stable Polymers", 2nd ed., Plenum, New York, 1987.
3. D. T. Grubb, I. Mita, and D. Y. Yoon, "Materials Science of High Temperature Polymers for Microelectronics", vol. 227, Pittsburgh, Material Research Society, 1991.
4. D. Wilson, H. D. Stenzenberger, and P. M. Hergenrother, "Polyimides", Blackie & Son Ltd., New York, 1990.
5. C. J. Feger, M. M. Khojasteh, and J. E. McGrath, "Polyimides : Materials, Chemistry, and Characterization", Elsevier Science Publishers B. V., Amsterdam, N. Y., 1989.
6. J. H. Lupinski and R. S. Moore, "Polymeric Materials for Electrics Packaging and Interconnection", ACS Symposium Series 407, American Chemical Society, Washington, D. C., 1989.
7. C. E. Sroog, *Prog. Polym. Sci.*, **16**(4), 561 (1991).
8. E. I. Du Pont de Nemours and Co.
9. R. S. Irwin and C. E. Smullen, U. S. Patent 4,640,972 (1987).
10. M. M. Koton, Br. Patent 1,183,306 (1970).
11. M. M. Koton, Br. Patent 2,025,311 (1980).
12. D. Jinda, T. Matsuda, and K. Sakamoto, *Sen. Gakkaishi*, **40**(12), 42 (1984).
13. L. M. Alberino, W. J. Farrissey, and J. S. Rose, U. S. Patent 3,708,458 (1973).
14. W. J. Farrissey and B. K. Onder, U. S. Patent 3,985,934 (1976).
15. H. Makino, Y. Kusuki, To. Harada, and H. Shimazaki, U. S. Patent 4,370,290 (1983).
16. T. Sasaki, H. Hatani, M. Kashima, H. Yoshimoto, and Y. Sasaki, U. S. Patent 4,247,443 (1981).
17. T. Kaneda, T. Katsura, K. Nakagawa, H. Makino, and M. Horio, *J. Appl. Polym. Sci.*, **32**, 3138 (1986).
18. S. Lee and F. W. Haris, submitted to *Polymer*, 1995.
19. H. G. Rogers, R. A. Gaudiana, W. C. Hoolinsed, P. S. Kalyanarman, J. S. Manello, C. McGowan, and R. Sahatjian, *Macromolecules*, **18**, 1058 (1985).
20. D. F. DeTar, *J. Org. Chem.*, **45**, 5166 (1980).
21. D. F. DeTar, *J. Am. Chem. Soc.*, **102**, 7988 (1980).