Synthesis and Characterization of Polyimide Fibers

Sangkug Lee
R & D Center, SKC Limited,
460 Chonhung-Ri, Songgo-Ub, Chonan 333-830, Korea
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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.1,2 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.3-7 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.\textsuperscript{8} to market the first industrial polyimide film, Kapton\textsuperscript{9}, which was prepared from 4,4'\textsuperscript{-diaminodiphenyl ether (ODA)} and pyromellitic dianhydride (PMDA). Irwin et al.\textsuperscript{9} 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.\textsuperscript{10,11} 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.\textsuperscript{12} 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 are also unstable and must be stored and handled with care.

Farrissey et al.\textsuperscript{13,14} 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\textsuperscript{5}, had tensile strengths and moduli of 2.65 g/d and 70 g/d, respectively. Makino et al.\textsuperscript{15} also polymerized 3,3',4,4'-biphenyltetra-carboxylic dianhydride (BPDA) and o-dianisidine in hot p-chlorophenol. 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.\textsuperscript{16} made this polymer by melt polymerization with an inherent viscosity of 0.85 dL/g. Kaneda et al.\textsuperscript{17} 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.\textsuperscript{18} However, the tensile strength of the fibers was 14.0 g/d, which was similar to the value obtained by the previous workers.\textsuperscript{17} 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 Chisakev 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 and was purified by recrystallization from a 1:1 (v/v) mixture of CHCl3 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 ± 0.1°C. Differential scanning calorimetry (DSC) analyses were performed in nitrogen with a heating rate of 20°C/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°C/min. Thermal mechanical analysis (TMA) analyses were performed in nitrogen using a heating rate of 10°C/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 8×10⁻⁴ s⁻¹ and a 22mm long drawn fiber at 25°C on a Rheometrics solid state analyzer RSA II.

**Polymerizations.**

**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°C and then heated gradually under nitrogen to 210°C. Isoquinoline (10 drops) was added at 180°C. The mixture was stirred and heated at 210°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 polymer was collected by filtration and dried under reduced pressure at 90°C for 24h.

**Fiber Spinning and Drawing Processes.** Polyimide fibers were spun from isotropic p-
chlorophenol solutions using a dry-jet wet spinning. The polyimide dope, which contained 6~
10% (w/w) solids and was obtained directly from the polymerization, was placed in the
bomb. After the bomb was heated to 60~110°C to afford a homogeneous solution, pressure
was applied to the piston to force the dope solution through the spinneret. The speed of the piston
movement was controlled by an Instron testing machine. The fibers were coagulated in a 1:1
mixture of water and ethanol and then taken up on a wheel. The speed of the take-up wheel was
controlled by a variable-speed motor. The fibers were immersed in ethanol for 3h in order to
extract residue p-chlorophenol. The fibers were then dried under reduced pressure at 150°C for
5h and then drawn to a draw ratio of 2.5 to 6.0 at 350~420°C.

RESULTS AND DISCUSSION

Polymer Syntheses and Properties.

Copolymerization of OTOL and ODA with
BPDA: In order to decrease the rate of crystal-
lization of fibers from 3,3′-dimethyl-4,4′-
diaminobiphenyl (OTOL) and 3,3′,4,4′-
biphenyltetra-carboxylic dianhydride (BPDA)
during drawing and, thus, increase the draw
ratio, OTOL (1) was copolymerized with various
amounts of 4,4′-diaminodiphenyl ether
(ODA) (2) in p-chlorophenol heated at reflux
(Scheme 1). The solvent contained a catalytic
amount of isoquinoline. The values for x and y
shown in Scheme 1 represent the feed ratios of
OTOL (1) to ODA (2) used in the copolymer-
izations. The solids concentration was varied
from 7 to 10% (w/w) (Table 1). The intrinsic
viscosities of copolymers 4a-d ranged from
4.35 dL/g to 5.43 dL/g in p-chlorophenol at
60°C.

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

<table>
<thead>
<tr>
<th>Copolyimide</th>
<th>Molar Ratio of Monomers</th>
<th>Monomer Concentration (wt%)</th>
<th>[η]a (dl/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>OTOL</td>
<td>ODA</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4a</td>
<td>8</td>
<td>2</td>
<td>7</td>
</tr>
<tr>
<td>4b</td>
<td>6</td>
<td>4</td>
<td>8</td>
</tr>
<tr>
<td>4c</td>
<td>4</td>
<td>6</td>
<td>9</td>
</tr>
<tr>
<td>4d</td>
<td>2</td>
<td>8</td>
<td>10</td>
</tr>
</tbody>
</table>

[a] Intrinsıc viscosity determined in p-chlorophenol at 60°C.

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

<table>
<thead>
<tr>
<th>Copolyimide</th>
<th>Molar Ratio of Monomers</th>
<th>TGAa</th>
<th>TMA</th>
</tr>
</thead>
<tbody>
<tr>
<td>OTOL</td>
<td>ODA</td>
<td>N2</td>
<td>Air</td>
</tr>
<tr>
<td>4a</td>
<td>8</td>
<td>565</td>
<td>465</td>
</tr>
<tr>
<td>4b</td>
<td>6</td>
<td>567</td>
<td>460</td>
</tr>
<tr>
<td>4c</td>
<td>4</td>
<td>568</td>
<td>528</td>
</tr>
<tr>
<td>4d</td>
<td>2</td>
<td>572</td>
<td>561</td>
</tr>
</tbody>
</table>

[a] Temperature at which 5% weight loss occurred with a heating rate of 10°C/min.
[b] 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.
[c] Coefficient of thermal expansion(10^-5 °C^-1). The CTE values were determined as the mean between 50 and 200°C.
[d] 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 1Mpa, showed changes in slope in nitrogen between 276°C and 280°C (Fig. 4). The 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. 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.
Fig. 3. DSC thermogram of copolyimide 4b obtained in nitrogen with a heating rate of 20°C/min.

<table>
<thead>
<tr>
<th>Table 3. Preparation and Properties of Fibers of 4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Copoly-</td>
</tr>
<tr>
<td>imide</td>
</tr>
<tr>
<td>(°C)</td>
</tr>
<tr>
<td>4a</td>
</tr>
<tr>
<td>4b</td>
</tr>
<tr>
<td>4c</td>
</tr>
<tr>
<td>4d</td>
</tr>
</tbody>
</table>

*a 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
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 copolymerization.

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

<table>
<thead>
<tr>
<th>Copolyimide</th>
<th>Molar Ratio of Monomers</th>
<th>Monomer Concentration (wt%)</th>
<th>[η]b (dL/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>6a</td>
<td>8</td>
<td>2</td>
<td>6</td>
</tr>
<tr>
<td>6b</td>
<td>6</td>
<td>4</td>
<td>7</td>
</tr>
<tr>
<td>6c</td>
<td>4</td>
<td>4</td>
<td>9</td>
</tr>
<tr>
<td>6d</td>
<td>2</td>
<td>8</td>
<td>10</td>
</tr>
</tbody>
</table>

a Intrinsic viscosity determined in p-chlorophenol at 60°C.

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

<table>
<thead>
<tr>
<th>Copolyimide</th>
<th>Molar Ratio of Monomers</th>
<th>TGAa</th>
<th>TMA</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>OTOL PFMB</td>
<td>N2</td>
<td>Air</td>
</tr>
<tr>
<td>6a</td>
<td>8</td>
<td>2</td>
<td>571</td>
</tr>
<tr>
<td>6b</td>
<td>6</td>
<td>4</td>
<td>582</td>
</tr>
<tr>
<td>6c</td>
<td>4</td>
<td>6</td>
<td>596</td>
</tr>
<tr>
<td>6d</td>
<td>2</td>
<td>8</td>
<td>600</td>
</tr>
</tbody>
</table>

a Temperature at which 5% weight loss occurred with a heating rate of 10°C/min.
b 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.
c Coefficient of thermal expansion (x10−5 °C−1). The CTE values were determined as the mean between 50 and 200°C.
d Could not be detected with DSC.

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. 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, 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 $3.2 \times 10^{-5} \text{°C}^{-1}$ (Table 5). The CTE coefficients increased as the copolymers' PFMB content increased. This is further evidence that

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

<table>
<thead>
<tr>
<th>Copolyimide</th>
<th>Dope Temp. (°C)</th>
<th>Drawing Temp. (°C)</th>
<th>Drawing ratio</th>
<th>Denier</th>
<th>Fibers* T/E/M</th>
</tr>
</thead>
<tbody>
<tr>
<td>6a</td>
<td>60</td>
<td>420</td>
<td>4.5</td>
<td>19.0</td>
<td>15.10/2.10/722</td>
</tr>
<tr>
<td>6b</td>
<td>60</td>
<td>420</td>
<td>6.0</td>
<td>7.5</td>
<td>10.60/1.84/574</td>
</tr>
<tr>
<td>6c</td>
<td>60</td>
<td>420</td>
<td>6.0</td>
<td>5.7</td>
<td>13.46/1.66/810</td>
</tr>
<tr>
<td>6d</td>
<td>60</td>
<td>420</td>
<td>6.0</td>
<td>6.8</td>
<td>12.37/2.29/566</td>
</tr>
</tbody>
</table>

*T = Tensile strength (g/d); E = Elongation at break (%); M = Modulus (g/d).

Fig. 8. TGA thermograms of copolyimides 4a-b obtained in nitrogen with a heating rate of 10°C/min.

The incorporation of PFMB in the copolyimers 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. The fibers were drawn to higher draw ratios than could be obtained with copolyimide 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 at 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

2. M. I. Bessonov, M. M. Koton, V. V.