

# Morphology of Polyimide Fibers Derived from 3,3',4,4'-Biphenyltetracarboxylic Dianhydride and 4,4'-Oxydianiline

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**ABSTRACT:** As one member of high performance fibers, aromatic polyimide fibers possess many advantages, such as high strength, high modulus, high and low temperature resistance, and radiation resistance. However, the preparation of the high performance fibers is so difficult that the commercial fibers have not been produced except P84 with good flame retardancy. In this report, a polyimide was synthesized from 3,3',4,4'-biphenyltetracarboxylic dianhydride (BPDA) and 4,4'-oxydianiline (ODA) and the fibers were prepared from its solution by a dry-jet wet-spinning process. The formation of the as-spun fibers in different coagulation bath composition was discussed. Scanning electron microscope (SEM) was employed to study the morphology of the

as-spun fibers. As a result, the remnant solvent existed in the as-spun fibers generated from coagulation bath of alcohol and water. There were many fibrils and microvoids with the dimension of tens of nanometers in the fibers. One could observe the obvious fibrillation and the drawn fibers. The measurement for the mechanical properties of the fibers with a drawing ratio of 5.5 indicated that tensile strength and initial modulus were 2.4 and 114 GPa, respectively. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 93: 669–675, 2004

**Key words:** polyimides; high performance polymers; fibers; morphology

## INTRODUCTION

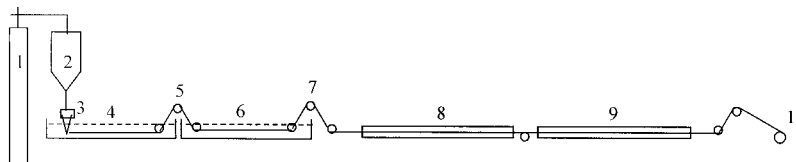
The demands of the market for high performance fibers are for “faster, stronger, lighter, safer” textiles. Fortunately, high performance and high temperature resistant fibers have been developed to aid in allowing products to meet these challenges. High performance polymeric fibers with high strength and modulus, high temperature resistance, and excellent flame retardancy for use in engineering applications such as high performance composites have undergone significant developments in the last two decades.<sup>1</sup> One example is the production of aromatic polyamides (aramids) such as poly(*p*-phenylene terephthalamide) (Kevlar<sup>®</sup> or Twaron<sup>®</sup>), which can be made by the spinning of liquid-crystalline solution.<sup>2–4</sup> There is now considerable interest in producing a heterocyclic rigid-rod polymer, again by spinning from liquid-crystalline solutions. High-treated fibers of poly(*p*-phenylenebenzobisthiazole) (PBZT) have been produced with tensile modulus values of 320 GPa. This may be compared with a value of 370 GPa obtained for poly(*p*-phenylene benzobisoxazole) (PBO) fibers.<sup>5,6</sup> Recently, AKZO

NOBEL<sup>7–9</sup> has developed a new rigid-rod polymer fiber, poly(2,6-diimidazo(4,5-*b*:4',5'-*e*)pyridinylene-1,4(2,5-dihydroxy) phenylene) (PIPD), called M5. The Young's modulus and tensile strength for the PIPD or M5 fibers have been determined to be greater than 300 and 4 GPa, respectively, and the limiting oxygen index (LOI) is more than 50.<sup>10</sup>

As one type of high performance polymers, polyimides have been focused on by researchers since the 1960s in that they have high mechanical properties, high temperature resistant, excellent radiation resistance, etc. A significant amount of technology has been developed such that polyimides have been found in widespread commercial use, such as adhesives, coatings, composite matrices, fibers, films, foams, membranes, and moldings.<sup>11</sup>

Generally, the preparation of polyimide fibers includes two types: a two-step process and a one-step process. In the two-step process, the soluble polyamic acids (PAAs) derived from a dianhydride and diamine in a polar solvent are spun into coagulation to prepare PAAs fibers. The next step is that PAAs fibers are converted to the polyimide by thermal imidization via heating or by chemical imidization via dipping the product in a solution with acetic anhydride, pyridine, or triethyl amine.<sup>12–14</sup> Irwin et al.<sup>15</sup> prepared the poly-pyromellitimide fibers in this manner. The precursor fibers from polyamic acid solutions were thermally

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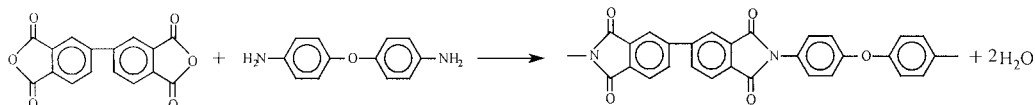
**Scheme 1** Flow process diagram of spinning polyimide fibers. 1, nitrogen gas with 0.5 MPa; 2, polyimide solution; 3, spinning spinneret with 12 holes; 4, coagulation bath with a mixture solution of water and alcohol (1 : 1); 5 and 7, rollers; 6, washing bath, water; 8, heating tube with  $220 \pm 3^\circ\text{C}$ ; 9, heating tube with  $340 \pm 5^\circ\text{C}$ ; 10, taking up.

converted *in situ* to the corresponding polyimide fibers. The fibers showed excellent high temperature performance, but the tenacity and initial modulus were limited to small values. Dorogy and St. Clair<sup>16,17</sup> reported that PAA could be synthesized from 3,3',4',4'-benzophenonetetracarboxylic dianhydride (BTDA) and 4,4'-oxydianiline (ODA) in DMAc and PAA fibers could be obtained by spinning the dopes into alcohol or glycol. The fibers then were thermally imidized into polyimide fibers. Presently, a polyimide fiber named P84 has been produced by A. G. Leizing by means of a two-step spinning process. However, the main characteristic of P84 is temperature resistance and flame retardancy.<sup>18</sup>

Although the products of polyimides are mostly manufactured by the two-step technique described above, it is desirable to prepare high-molecular aro-

matic polyimides in a one-step process.<sup>19</sup> Kaneda et al.<sup>20,21</sup> reported that polyimide solution could be prepared in the one-step polycondensation reaction of a dianhydride with various aromatic diamines in *p*-chlorophenol and the solution dopes were directly used to produce polyimide fibers. The spinning, drawing, and thermal process could be conducted on one line. Cheng and coworkers<sup>22-24</sup> prepared a series of polyimide fibers with high strength (3.1 GPa) and high modulus (120 GPa) by on-step technology. However, in a one-step process, it is difficult to eliminate the remnant solvent from the as-spun fibers, such as *p*-chlorophenol or *m*-cresol.

One type of polyimide from BPDA and ODA has been synthesized by a one-step process in *p*-chlorophenol, which is simply schemed as follows:



Polyimide fibers have been prepared by a dry-jet wet-spinning process and then the as-spun fibers have been treated in heating tubes. In this report, the spinning technology, morphology of as-spun fibers, and the mechanical properties are discussed.

## EXPERIMENTAL

### Materials

3,3',4,4'-Biphenyltetracarboxylic dianhydride was supplied by Shanghai Resin Institute of China and was recrystallized prior to use. 4,4'-Oxydianiline purchased from Shanghai Chemical Reagents Co. was used as received. *p*-Chlorophenol supplied by Shanghai Chemical Reagents Co. was recrystallized prior to use.

### Synthesis of polyimide

Polyimide was synthesized in our laboratory in *p*-chlorophenol at elevated temperatures via one-step polymerization. The polyamic acid precursors were not isolated. In a 100-mL round-bottom flask

equipped with a nitrogen inlet and a stir bar, a condenser was charged with 2 g 4,4'-ODA and 50 mL *p*-chlorophenol. The solution was stirred until the diamine completely dissolved, and then 2.94 g BPDA was added slowly into this solution. The reaction was carried out at  $150^\circ\text{C}$  in refluxing solvent for 2 h and the water produced from the polycondensation reaction was removed from the condenser. The system then was heated to  $200^\circ\text{C}$  and continued to react for 4 h. The concentration of polyimide in the solvent was about 10% (w/v). The concentrated solution was solid at room temperature and it became viscous dope when it was heated to  $70^\circ\text{C}$  or higher.

### Preparation of polyimide fibers

The polymer solution was filtrated and degassed at  $100^\circ\text{C}$ . Fibers was conducted on a spinning machine which was home designed as shown in Scheme 1.

The dopes at  $100^\circ\text{C}$  were spun into a coagulation bath by a dry-jet wet-spinning process with a gas gap of 20 mm. The composition of the bath was water and alcohol. The as-spun fibers entered into the second

TABLE I  
Effect of Coagulation Bath Composition on Formation of As-Spun Fibers

Coagulation bath composition (alcohol/water, v/v)	Phenomenon
100/0	Formation of as-spun fibers was too fast, and the fibers were too fragile to be drawn in the heating tubes
70/30	Formation of as-spun fibers was available, but the drawing properties of the fibers in the heating tubes were not good
50/50	Good formation of as-spun fibers was valuable for the drawing process
30/70	The as-spun fibers could form, but the solidification of the dope solution in the coagulation bath is so slow that the as-spun fibers including 12 the filaments easily bound together because of more remnant solvent in the fibers
0/100	Nonformation

bath (washing bath, alcohol). The drawing procedure was conducted on two heating tubes as shown in Scheme 1. The temperatures of the two stainless steel tubes were  $220 \pm 3$  and  $340 \pm 5^\circ\text{C}$ , respectively.

### SEM

As-spun polyimide fibers could be obtained at roller 5 (as shown in Scheme 1). Alcohol, water, and solvent on the surface of the fibers were immediately sucked using filter paper. The as-spun fibers were broken in liquid nitrogen to minimize the effect on the morphology of the fibers. The broken fibers were embedded using celloidin ether solution. The samples were gold-sputtered when the ether vaporized up. A JSM-5600LV scanning electron microscope was employed to observe the cross section of the fibers at an accelerating voltage of 10 KV. Since the drawing fibers could not be broken in liquid nitrogen, the single fiber had to be drawn to break in liquid nitrogen or was cut using a sharp cutter.

### Mechanical properties

Diameters of the as-spun or the drawn monofilament were observed and recorded on an optical microscope with a scale. The measurement of mechanical properties was carried out on Shimadzu AGS-500ND instrument made in Japan. More than 10 monofilaments for one sample were tested and the average data were used to characterize the mechanical properties of the sample.

## RESULTS AND DISCUSSION

### Formation of the as-spun fibers

The as-spun fiber structure generated in a wet spinning coagulation bath is a result of the counterdiffusion of solvent and nonsolvent and the phase separation of the solution. The concentration of coagulation

bath is one of the factors affecting the as-spun fiber structure. In this spinning experiment, we selected a mixture of alcohol and water as the coagulation bath because alcohol could dissolve the solvent *p*-chlorophenol but water could not. One found that the solidification rate of the dope solution in a coagulation bath of 100% alcohol was so fast that the fibers generated in this coagulation bath composition were too fragile. Therefore, water should be added into the coagulation bath to control the formation rate or solidification rate of the as-spun fibers. In the spinning process, we found that the coagulation bath composition had an obvious influence on the formation of as-spun fibers. Some phenomena of the formation of the as-spun fibers are listed in Table I. The five coagulation bath compositions listed in Table I indicate that the composition of 50/50 (alcohol/water) was the best value for the formation of the as-spun fibers and for the drawing process of the fibers in the heating tubes.

The as-spun fibers generated from the coagulation bath still remained more solvent (*p*-chlorophenol) in the fibers. The as-spun fibers were immersed in pure

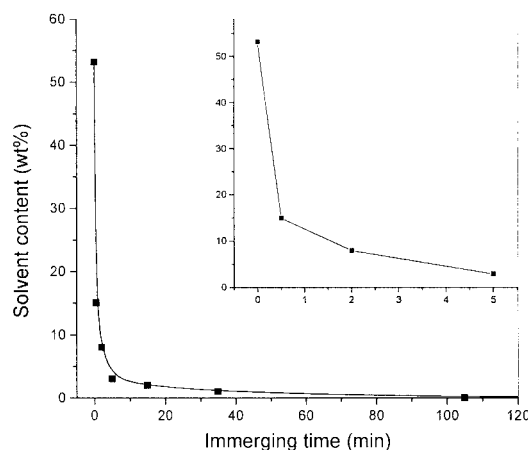
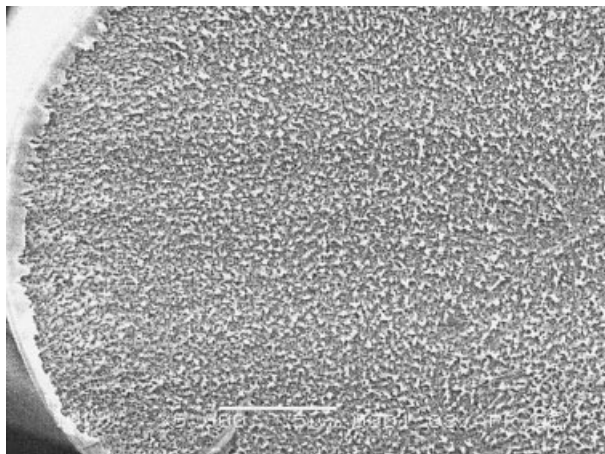


Figure 1 The change of solvent content with the immersion time of the as-spun fibers in alcohol.



**Figure 2** SEM image of the cross section of an as-spun monofilament generated from a coagulation bath of 50/50 (alcohol/water).

alcohol for some time to eliminate the remnant *p*-chlorophenol from the fibers. As one sample, the as-spun fibers generated from the coagulation bath composition of 50/50 (alcohol/water) were immersed in alcohol. They were taken out after some time and the liquid on the surface were immediately sucked using filter paper. The weight change with the immersion time was recorded. As shown in Figure 1, it would take more than 5 min to eliminate the remnant solvent in the as-spun fibers. Since the spinning rate was more than 5 m/min, it was impossible to eliminate the remnant solvent via increasing the length of the washing bath filled with 100% alcohol. Therefore, the heating tubes were employed to eliminate the remnant solvent in the as-spun fibers. As shown in Scheme 1, the first heating tube (No. 8) with a temperature of about 220°C eliminated the remnant solvent.

### Morphology of the fibers

Figure 2 shows a micrograph of the cross section of the as-spun fibers. The image indicated the cross section of the fibers was a regular circle even if it was broken in liquid nitrogen. Moreover, it was found that there were many "light dots" with the dimension of tens of nanometers. The light dots were considered to be the crystals of *p*-chlorophenol (m.p. 39°C) remaining in the as-spun fibers. To further explain it, the as-spun fibers were washed in alcohol for 2 h and the sample was observed again on SEM. As shown in Figure 3, the images with different magnification indicated that the light dots disappeared and the cross section of the monofilament was still a regular circle. Surprisingly, lots of fibrils and microvoids with the dimension of tens nanometer existed in the fibers.

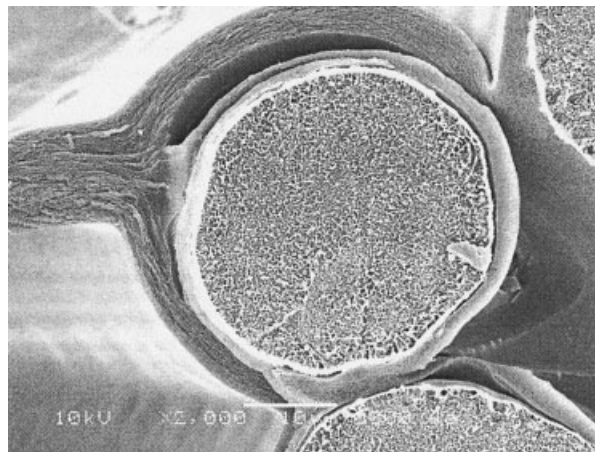
Figure 4 shows images of the cross section of an as-spun monofilament generated from a different co-

agulation bath composition. Contrasting the two micrographs, it was found that the concentration of the coagulation bath had little influence on the morphology of the as-spun fibers. The void size had no obvious differences. This was not in line with Fick's law of diffusion.

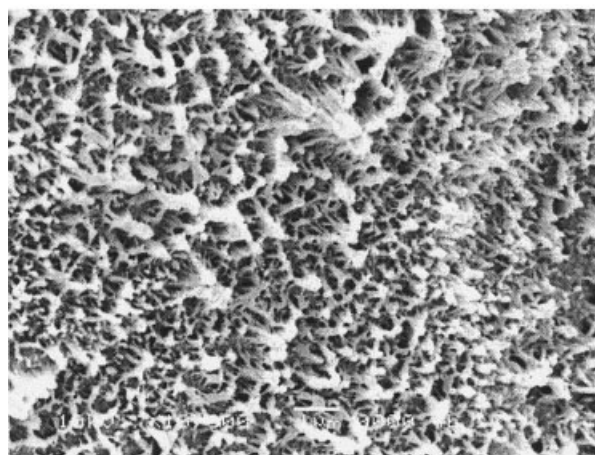
According to Fick's law of diffusion, the void size in as-spun fibers can be analyzed by the rate of diffusion and phase separation.

$$J_i = -D_i \frac{dC_i}{dx} \quad (1)$$

where,  $J_i$  is flux of component  $i$ ,  $D_i$  is diffusion coefficient of component  $i$ , and  $dC_i/dx$  is gradient of concentration of component  $i$  in a coagulation bath. The

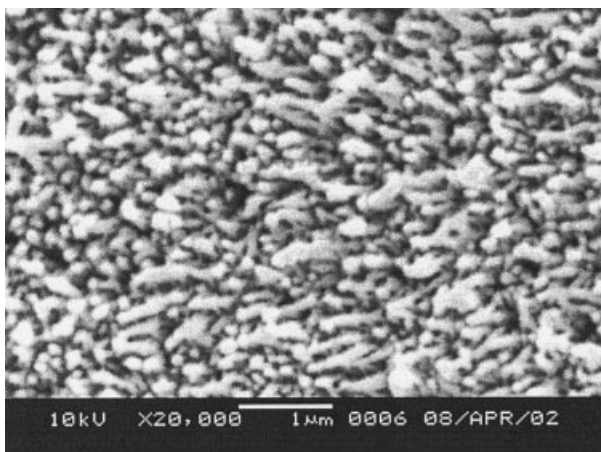


(a)

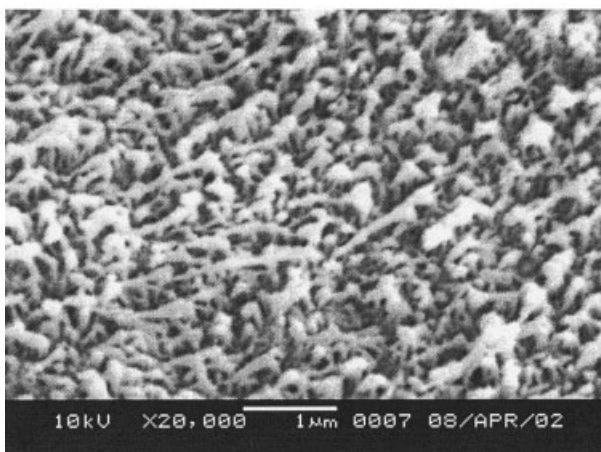


(b)

**Figure 3** SEM images of a cross section of a monofilament immersed in alcohol for 2 h: (a)  $\times 2,000$ ; (b)  $\times 10,000$ .



(a)



(b)

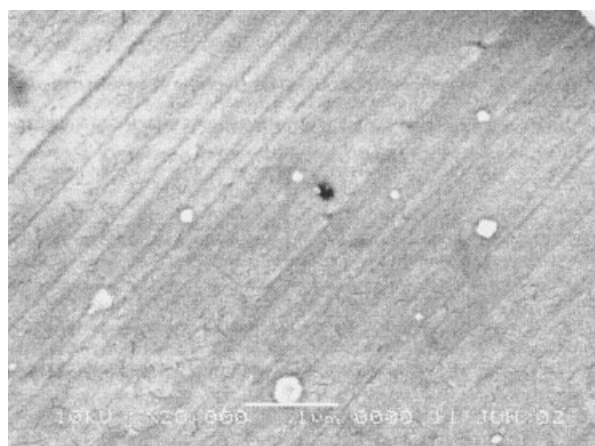
**Figure 4** SEM images of a cross section of the as-spun fibers generated from different coagulation bath compositions of alcohol to water: (a) 100/0; (b) 50/50.

change of diffusion coefficient  $D_i$  or the gradient of concentration  $dC_i/dx$  affected the rate of diffusion controlled by flux  $J_i$ . In fact, the changes of the coagulation bath composition were equal to the changes of  $dC_i/dx$ , so the flux  $J_i$  correspondingly changed, which resulted in different void size. Some formation of fibers from the polymer/solvent/nonsolvent system obey Fick's law of diffusion, such as the PAN/NaSCN/H<sub>2</sub>O system used to manufacture PAN fibers and the polyaniline(PANI)-polyamide11/H<sub>2</sub>SO<sub>4</sub>/H<sub>2</sub>O system used to prepare conductive PANI-PA11 blend fibers.<sup>25</sup>

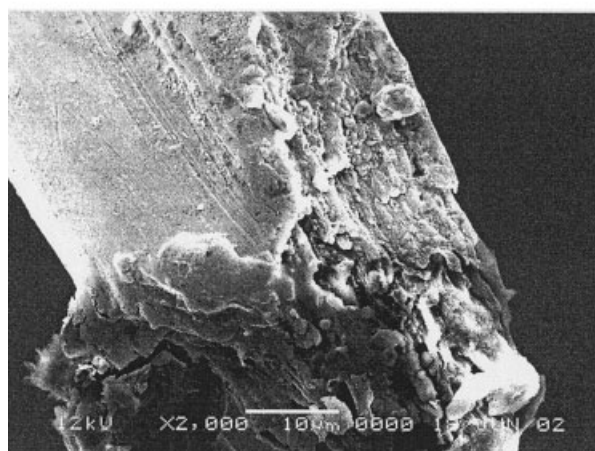
Both Figures 3 and 4 show that the fibrillation took place in the as-spun fibers. There were lots of fibrils with the dimension of tens of nanometers. The fibrils looked like "ultrafine fibers" drawn from the as-spun fibers, which consisted of a monofilament. One also

observed lots of voids on the micrographs of the cross section. The void size was also the magnitude of tens of nanometers. As to how to form the fibrils and the voids and how they affect the heating treatment process and the mechanical properties, further detailed study is necessary.

As one member of high performance fibers, polyimide fibers possessed not only high temperature resistance, but low temperature resistance. The drawn fibers via heating tubes could not be broken in liquid nitrogen because of the macromolecular orientation along the axial. Therefore, two methods were utilized to break the drawn fibers. One was cutting the monofilament using a sharp cutter, and the other was drawing the monofilament to break in liquid nitrogen. SEM images of the cross section are shown in Figures 5(a)



(a)



(b)

**Figure 5** (a) SEM image of the cut section of the drawn monofilament. (b) SEM image of the fractured section of the drawn monofilament.

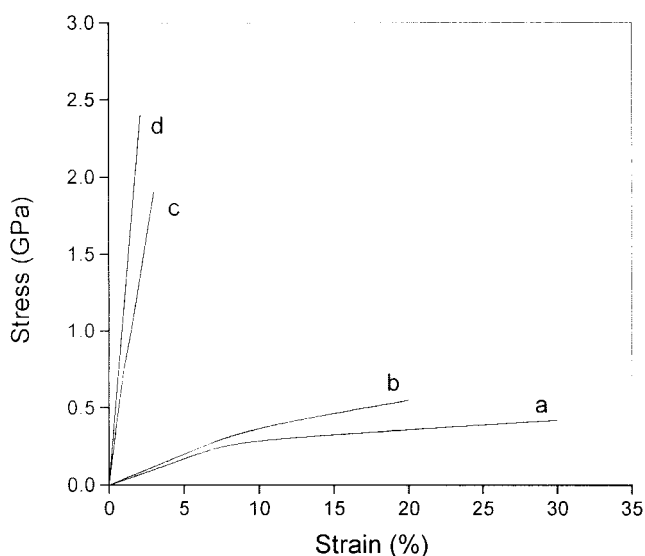
and (b), respectively. There were many obvious cutting traces on the sample, so little available information could be obtained from Figure 5(a).

However, the fractured sample, shown in Figure 5(b), indicated that the fibrillation still existed in the fibers but was not as obvious as the as-spun fibers. The fractured section of the drawn fibers at low temperature (liquid nitrogen) was not fragile, which was very different from current polymeric fibers such as PP and PET fibers. The phenomena further verified the low temperature resistance of the BPDA-ODA fibers.

### Mechanical properties

The fiber diameters necessary for initial modulus and tensile strength calculations were obtained from an optical microscope with a scale. To minimize the effect of the differences of the diameters of the fibers on the mechanical properties, the diameter of a separate monofilament was measured and then the monofilament was tested on a forcing instrument and the mechanical properties were recorded. Measurements of at least 10 single filaments for one sample were employed to calculate the mechanical properties.

Figure 6 shows typical stress-strain curves for the BPDA-ODA fibers and Table II lists the data of tensile strength, modulus, and elongation of the fibers. Curve (a) in Figure 6 indicates that the as-spun fibers possessed poorer mechanical properties. When the as-spun fibers were immersed in alcohol to eliminate the remnant *p*-chlorophenol, the tensile strength would increase by a little, as shown in curve (b). The yielding process took place at the elongation of  $\sim 7\%$  for the



**Figure 6** Tensile stress-strain curves for the polyimide fibers: (a) as-spun fibers; (b) as-spun fibers immersed in alcohol for 1 h; (c) drawn fibers with a draw ratio of 3; (d) drawn fibers with a draw ratio of 5.5.

**TABLE II**  
Mechanical Properties of BPDA-ODA Fibers

Samples	Tensile strength (GPa)	Initial modulus (GPa)	Elongation to break (%)
As-spun fibers	0.42	33	30
As-spun fibers immersed in alcohol for 1 h	0.55	40	21
Drawn fibers (3 times)	1.9	75	2.9
Drawn fibers (5.5 times)	2.4	114	2.1

as-spun fibers. However, the yielding process did not take place for the drawn fibers, which shown in Figure 6 (curves c and d). The tensile strengths of the drawn fibers with drawing ratios of 3 and 5.5 were up to 1.9 and 2.4 GPa, respectively, and the Young's moduli were up to 75 and 114 GPa, respectively. These data indicate that it is possible to prepare polyimide fibers with high strength and high modulus via a one-step spinning process even if the mechanical properties need to improve further.

### CONCLUSION

The polyimide fibers of BPDA-ODA were prepared by a dry-jet wet-spinning process. The investigation on the formation of the fibers indicated that the as-spun fibers generated from the coagulation bath composition of alcohol and water (50/50) were available for heat drawing and heat treatment. There were many fibrils and microvoids with the dimension of tens of nanometers in the fibers. The coagulation bath composition had little influence on the microvoids, which did not coincide with Fick's law of diffusion. The fibrillation took place in both the as-spun fibers and the drawing fibers. The BPDA-ODA fibers drawn in heating tubes had a high tensile strength of 2.4 GPa and a high initial modulus of 114 GPa even if the as-spun fibers did not possess good mechanical properties.

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