

Synthesis and Properties of Homopolyamide and Copolyamides Fibers Based on 2,6-Bis(*p*-aminophenyl)benzo[1,2-*d*;5,4-*d'*]bisoxazole

Xiangqun Q. Chen,¹ Qiu Sun,² Yudong Huang,² Wei Cai¹

¹Postdoctoral Station of Materials Science and Engineering, School of Materials Science and Engineering, Harbin Institute of Technology, Harbin 150001, People's Republic of China

²Department of Applied Chemistry, Harbin Institute of Technology, Harbin 150001, People's Republic of China

Received 21 October 2007; accepted 2 June 2008

DOI 10.1002/app.28811

Published online 30 July 2008 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: A novel aromatic homopolyamide with benzobisoxazole units in the main chain was synthesized with 2,6-bis(*p*-aminophenyl)benzo[1,2-*d*;5,4-*d'*]bisoxazole and terephthaloyl chloride by low temperature solution polycondensation, the inherent viscosity of which was 1.98 dL/g. The diamine and *p*-phenylenediamine with terephthaloyl chloride were used to synthesize the copolyamides. The structures of homopolyamide and copolyamides were characterized by IR spectra, elemental analysis, and wide-angle X-ray diffraction. Wide-angle X-ray diffraction measurements showed that homopolyamide and copolyamides were predominantly crystalline. The results of thermal analysis indicated that the thermal stabilities of the copolymer increased with an increase of the molar fraction of benzobisoxazole in the copolymers. The thermal stability of the copolyamides with decomposition

temperatures (at 10% weight loss) above 570°C was better than that of poly(*p*-phenylene terephthalamide) (PPTA). Fibers of homopolyamide and copolyterephthalamides were spun from lyotropic liquid crystal dope in 100% H₂SO₄. When compared with PPTA fibers prepared under the same conditions, the tensile strengths of copolyamides fibers improved by 20–33% with tensile strengths of 1.81 GPa, tensile moduli of 76 GPa, and elongations at break of 3.8–4.1%, which indicated that copolyamides fibers had outstanding mechanical properties. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 110: 1891–1898, 2008

Key words: PPTA fiber; copolyamide; 2,6-bis(*p*-aminophenyl)benzo[1,2-*d*;5,4-*d'*]bisoxazole; mechanical properties; thermal properties

INTRODUCTION

Poly(*p*-phenylene terephthalamide) (PPTA) with excellent mechanical properties and high thermal properties can be used in many industrial applications such as aerospace materials, high strength and modulus fibers, protective coatings or as separation membranes.¹ Fibers obtained from anisotropic solution of PPTA have been used in applications for which high thermal stability and mechanical strength are required.² At present, many efforts have been made with the aim of designing the chemical structure to obtain aramids that are processable by conventional techniques. One successful approach is to introduce flexible linkages into polymer backbone to increase the solubility.³ These modifications suppress the melting temperature and lead to soluble

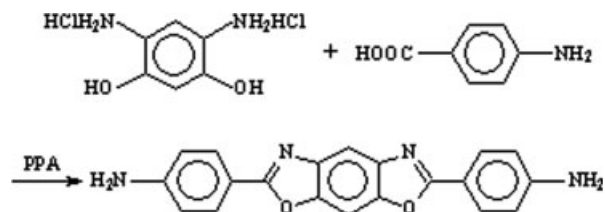
and amorphous polymers. Furthermore, the incorporation of bulky pendent groups can decrease hydrogen bonding and interchain interactions in polyamides and generally disturb the coplanarity of aromatic units to reduce packing density and crystallinity.⁴ Now there is a problem that these polymers could not be used as materials of fiber.

In Goto et al.⁵ work, poly(4,4'-diphenyl ether terephthalamide) was selected as a flexible segment for block copolymers of PPTA, the tensile strength of fiber was 130–500 MPa. For PPTA, many attempts have been made at crosslinking by using substituted terephthalic acids or *p*-phenylenediamines.^{6,7} No fibers of such polymers have been described; they could not be processed from sulfuric acid solutions due to the instability of the substituents towards this solvent. Rickert et al. used a new diamine, 2,2,6,6-tetraoxo-1,3,5,7-tetrahydro-2,6-dithia-s-indacene-4,8-diamine to copolymerize with *p*-phenylenediamine and terephthaloyl dichloride for the synthesis of thermally crosslinkable rigid-rod aramids.^{8,9} The fibers were comparable to PPTA fibers with respect to their mechanical behavior. The introduction of urea moieties in the main polyamide chain is a method to modify mechanical properties of the polymers.^{10,11}

Correspondence to: X.Q. Chen (chenxq@hit.edu.cn).

Contract grant sponsor: Heilongjiang Province Science Foundation for Youths; contract grant number: QC07C23.

Contract grant sponsor: The National Basic Research Program of China; contract grant number: 2006CB708609.



Scheme 1 Synthesis of 2,6-bis(*p*-aminophenyl)benzo[1,2-*d*;5,4-*d'*]bisoxazole.

Poly(benzo[1,2-*d*; 5,4-*d'*]bisoxazole-2,6-diyl-1,4-phenylene) (*cis*-PBO) with unique extended rigid-rodlike configuration show excellent thermooxidative stability, higher tensile properties, and higher hydrolytic stability.^{12,13} Because the incorporation of heterocycles such as oxadiazole or benzoxazole in the main chain of polymers usually results in copolymers with high thermal and oxidative stabilities and also influences solubility of polymer.^{14–17} These authors claimed that polymers with benzoxazole units, and particularly poly(amide-benzoxazole)s,^{18,19} seem to offer an interesting approach to special polymer materials. The mechanical performance of PPTA fiber is inferior to that of PBO, but the improvement on this aspect is seldom. In this paper, the structure unit of *cis*-PBO was added to the main chain of PPTA to enhance the thermal stability and mechanical property of PPTA fiber, without imparting solubility of PPTA.

EXPERIMENTAL

Materials

1,3-Diamino-4,6-dihydroxybenzene dihydrochloride, *p*-aminobenzoic acid, *p*-phenylenediamine, triethylamine, terephthaloyl dichloride, anhydrous lithium chloride, and *N*-methyl-2-pyrrolidone (NMP) were analytical grade. NMP was purified by distillation under reduced pressure prior to use. Triethylamine was used after distillation in the presence of sodium. *P*-phenylenediamine and terephthaloyl dichloride were purified by sublimation under reduced pressure prior to use. 2,6-Bis(*p*-aminophenyl)benzo[1,2-*d*;5,4-*d'*]bisoxazole was synthesized in my laboratory by a modified method.²⁰

Synthesis of 2,6-bis(*p*-aminophenyl)benzo[1,2-*d*;5,4-*d'*]bisoxazole

Under a nitrogen atmosphere, 17.85 g P₂O₅ were dissolved in 10.26 g H₃PO₄ and maintained at 150°C for 4 h to form polyphosphoric acid (PPA). After cooling to 120°C, 5 mmol of 1,3-diamino-4,6-dihydroxybenzene dihydrochloride was added, and then 10 mmol of *p*-aminobenzoic acid were added. The reaction mixture was maintained at 150–210°C for

about 10 h and then at 210°C for 4 h. After that, the mixture was poured into ice water, and the diamine obtained was washed with water, neutralized with sodium bicarbonate, and washed with water for several times. The isolated compound was a yellow powders, it was dried under vacuum for 6 h at 100°C (see Scheme 1).

Yield: 99% (1.695 g). mp: 414–415°C (DSC). FTIR (KBr, cm⁻¹): 3316 (*N*–H str.), 1622 (C=N of oxazole unit), 1282 and 1055 cm⁻¹ (C–O–C str.). Elem. Anal. Calcd for C₂₀H₁₄N₄O₂ (324.36): C, 70.16%; H, 4.13%; N, 16.36%. Found: C, 70.01%; H, 4.12%; N, 16.20%.

Synthesis of model compound

A flask equipped with dropping funnel was filled with a solution of 2,6-bis(*p*-aminophenyl)benzo[1,2-*d*;5,4-*d'*]bisoxazole (0.342 g, 1.0 mmol) and anhydrous lithium chloride (2 g) in 25 mL of NMP. Triethylamine (0.203 g, 2.0 mmol) was added in the solution. Benzoyl chloride (0.295 g, 2.1 mmol) diluted with NMP (10 mL) was added dropwise to the stirred solution at 0°C under nitrogen. The mixture was stirred at ambient temperature for 5 h in a stream of N₂. Then, it was poured into water to obtain yellow solid by filtered off. The yellow solid was extracted by acetone and dried to afford model compound.

Yield: 98% (0.539 g). mp: 446–452°C (DSC). FTIR (KBr, cm⁻¹): 3336 (*N*–H str.), 1652 (C=O), 1600 (C=N and aromatic), 1259 and 1054 cm⁻¹ (C–O–C str.). Elem. Anal. Calcd for C₃₄H₂₂N₄O₄ (550.57): C, 74.17%; H, 4.03%; N, 10.18%. Found: C, 73.89%; H, 4.34%; N, 10.33%.

Homopolymer synthesis

A flask equipped with a dropping funnel was charged with a solution of 2,6-bis(*p*-aminophenyl)benzo[1,2-*d*;5,4-*d'*]bisoxazole (0.342 g, 1.0 mmol) and anhydrous lithium chloride (2 g) in 25 mL of NMP. Triethylamine (0.203 g, 2.0 mmol) was added to the solution. Terephthaloyl dichloride (0.223 g, 1.1 mmol) dissolved in NMP (10 mL) was added dropwise to the stirred solution at 0°C under N₂. The mixture was subsequently stirred at ambient temperature for 30 min in a stream of N₂ and then stayed for 0.5 h. After reaction mixture was stirred rapidly, it was poured into ice water, and the yellow solid precipitate was filtered off, washed with water, and dried in a vacuum at 100°C, then extracted by acetone to afford the polymer.

Yield: 96% (0.453 g). FTIR (KBr, cm⁻¹): 3426 (*N*–H str.), 1652 (C=O), 1600 (C=N and aromatic), 1314 (*N*–H def.), 1314 (C–N str.), 1243, 1052 cm⁻¹ (C–O–C str.). Elem. Anal. Calcd for C₂₈H₁₆N₄O₄

TABLE I
Thermal and Tensile Properties of Copolymers

Polymer	Content of benbisoxazole (mol %)	η_{inh} (dL/g)	T_d (°C)	Weight loss at 700°C (%)	Tensile strength (GPa)	Elongation (%)	Modulus (GPa)
a	0	4.21	557	47	1.39	4.1	57
b	10	4.22	570	52.8	1.81	3.9	76
c	20	4.03	572	59.5	1.45	3.7	62
d	40	2.62	580	65	1.25	4.0	55
e	100	1.98	595	67	1.10	3.9	28.3

(472.46) C, 71.18%; H, 3.41%; N, 11.85%. Found: C, 69.51%; H, 3.66%; N, 10.93%.

Copolymer synthesis

As an example, the polymerization procedure of Copolymer 10 (contains 10 mol % of 2,6-bis(*p*-aminophenyl)benzo[1,2-*d*;5,4-*d'*]bisoxazole and 90 mol % of *p*-phenylenediamine) is described as follow.

A flask was filled with a solution of 2,6-bis(*p*-aminophenyl)benzo[1,2-*d*;5,4-*d'*]bisoxazole (0.0342 g, 0.1 mmol) and anhydrous lithium chloride (2 g) in 25 mL of NMP. Triethylamine (0.203 g, 2.0 mmol) was added to the solution. Terephthaloyl dichloride (0.0162 g, 0.08 mmol) was added to the stirred solution at 0°C under N₂. The mixture was vigorously stirred for 30 min. Then, *p*-phenylenediamine (0.972 g, 0.9 mmol) was added to the solution. After *p*-phenylenediamine was entirely soluble to the solution, terephthaloyl dichloride (0.186 g, 0.92 mmol) was added to the stirred solution. The mixture was subsequently stirred at ambient temperature for 30 min in a stream of N₂. Then, the mixture was stayed for 0.5 h. After reaction mixture was stirred rapidly for 5 min, it was poured into ice water, and the yellow solid precipitate was filtered off, washed with water, and dried in a vacuum at 100°C to afford the block copolymer (0.443 g, yield 96%). The molar ratio of the diamines and the inherent viscosities of the copolymers were presented in Table I.

Preparation of copolymer fiber

The copolymer powder was soluble into 100% H₂SO₄ to form an anisotropic reaction mixture at 20% solids content. The copolymer/H₂SO₄ dope was dry-jet wet spun using a piston-driven system specially designed for this purpose. For comparison, pristine PPTA polymerization and fiber spinning were carried out under the same conditions without adding 2,6-bis(*p*-aminophenyl)benzo[1,2-*d*;5,4-*d'*]bisoxazole. High-strength fibers can be produced by the spinning of liquid-crystalline solutions of copolyamides, homopolyamide, and PPTA in sulfuric acid. Solutions of 20% (weight ratio) polymer content in 100% H₂SO₄ were readily spun into fibers. The dopes at 80°C were spun into a coagulation

bath by a dry-jet wet-spinning process with a gas gap of 39 cm. The composition of the coagulation bath was water and draw ratio was 18.

Measurements

FTIR spectra were recorded on a Nicolet-Nexus 670 Fourier transform (FTIR) spectrophotometer. Inherent viscosity of the polymer was measured at a concentration of 0.5 g/dL in concentrated sulfuric acid at 25°C with a Ubbelohde viscometer. DSC and TG were performed at a heating rate of 10°C/min under flowing air with NETZSCH STA 449C thermal analyzer. The experiments were carried out using 10 mg samples. ¹H NMR spectra were obtained at 25°C in CF₃COOD solution with tetramethylsilane as an internal standard with a Bruker-AV 400 spectrometer. Elemental analysis was achieved on an Eager-300 elemental analyzer. Moreover, WAXD pattern was obtained for the powder specimen on a D/max-γB X-ray diffractometer using CuKα radiation (40 kV, λ = 0.1546 nm). The scanning rate was 0.02°/min over a range of 2θ = 10–40°. The liquid crystalline behavior of all polymer solution was studied by POM (POM3-X). And tensile tests were conducted by a staple fiber tensile tester (Lenzing VibrodynYG020C) with a gauge length of 2 cm and a strain rate of 2% min⁻¹.

RESULTS AND DISCUSSION

Single crystal analysis of 2,6-bis(*p*-aminophenyl)benzo[1,2-*d*;5,4-*d'*]bisoxazole

The single crystal of the diamine was grown during the slow crystallization of its NMP solution. Crystal

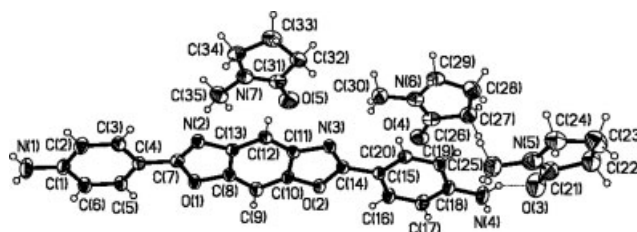
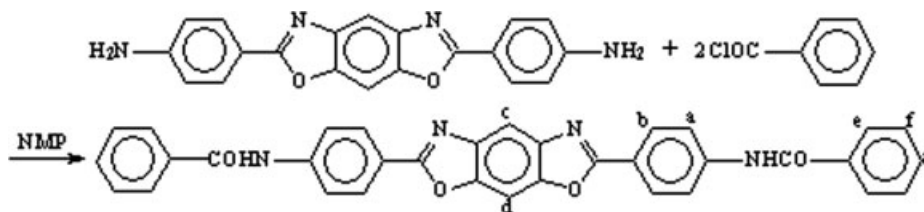


Figure 1 ORTEP diagram of 2,6-bis(*p*-aminophenyl)benzo[1,2-*d*;5,4-*d'*]bisoxazole determined by X-ray crystallography. All hydrogens have been omitted for clarity.



Scheme 2 Synthesis of model compound.

size of 0.65 mm × 0.38 mm × 0.18 mm was used for X-ray structure determination. Intensity data were collected on a Rigaku RAXIS-RAPID diffractometer at 293 K with graphite monochromatized Mo K α radiation ($\lambda = 0.071073$ nm). The structure was solved on a P4 computer with SHELXS-97 software. The molecular structure for the diamine was shown in Figure 1. The diamine crystallized in a triclinic system with space group $P\bar{1}$ [$M_w = 639.75$, $a = 0.75862(15)$, $b = 1.2525(3)$, $c = 1.7627(4)$ nm, $\alpha = 94.92(3)$, $\beta = 92.88(3)$, $\gamma = 99.19(3)$ where $D_c = 1.293$ g/cm 3 for $Z = 2$ and $V = 1.6438$ (6) nm 3]. Least-squares refinement based on 7333 independent reflections converged to final $R_1 = 0.0635$ and $R_w = 0.1501$.

The least-squares planes of the total molecule is $7.014x + 2.846y - 0.957z = 4.386$, and Rms deviation of fitted atoms is 0.00833 nm. The crystal structure of the diamine shows that the compound of plane structure has two kinds of intermolecular hydrogen bonds between the compound and NMP in the crystal. The ring of the monomer does not deviate significantly from the planar conformation. This will not disturb the coplanarity of aromatic unit to impart the solubility of formed copolyamides.²¹

Model reaction

To obtain fundamental information about the structure of polymer, the model compound was synthesized (Scheme 2) from 2,6-bis(*p*-amino-phenyl)benzo[1,2-*d*;5,4-*d'*]bisoxazole with benzoyl chloride and characterized by FTIR, ^1H NMR, and elemental analysis. In ^1H NMR spectrum of model compound (shown in Fig. 2), the resonance for the amino hydrogen disappeared, while a new singlet peak corresponding to amide protons of the model compound appeared at 8.48 ppm. And eight types of hydrogen atoms were well characterized in ^1H NMR spectrum.

Synthesis of the homopolymer and copolymers

Polyamide-benzoxazole was prepared by a low-temperature solution polycondensation technique²² in NMP from the diamine and terephthaloyl chloride

(Scheme 3), with LiCl as a solubility enhancer.^{23,24} Triethylamine was used to acid absorber to delete the by-product to develop molecular weight.²⁵ The inherent viscosity of the homopolymer was 1.98 dL/g.

In view of concentration of 2,6-bis(*p*-aminophenyl)benzo[1,2-*d*;4,5-*d'*]bisoxazole have an effect on molecular weight of copolyamides (see Scheme 4), the increase of the monomer concentration can suppress high molecular weight of products.²⁶ So all the polymerizations of copolyamides was conducted in lower 2,6-bis(*p*-aminophenyl)benzo[1,2-*d*;4,5-*d'*]bisoxazole content. Inherent viscosities of the copolyamides were in the range of 2.62 and 4.22 dL/g in 98% H $_2$ SO $_4$ at 25°C, shown in Table I.

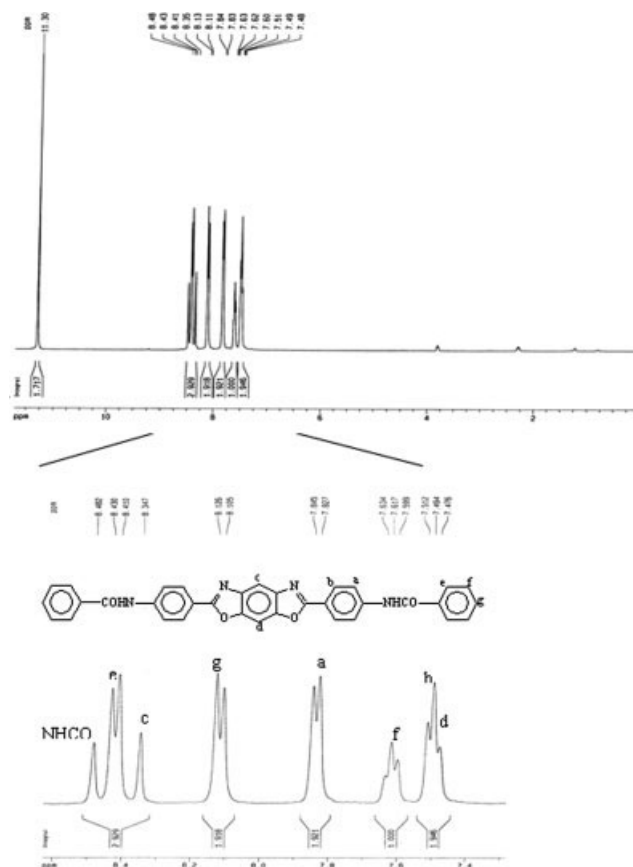
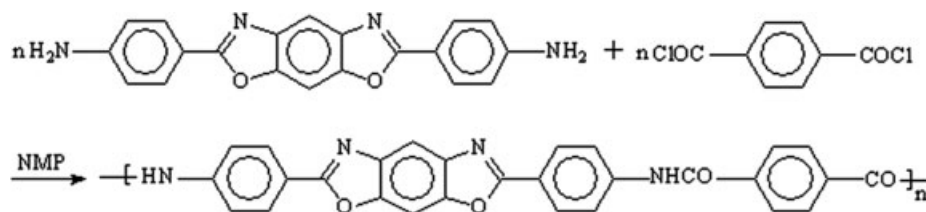


Figure 2 ^1H NMR spectrum of model compound in CF_3COOD .



Scheme 3 Synthesis of homopolyamide.

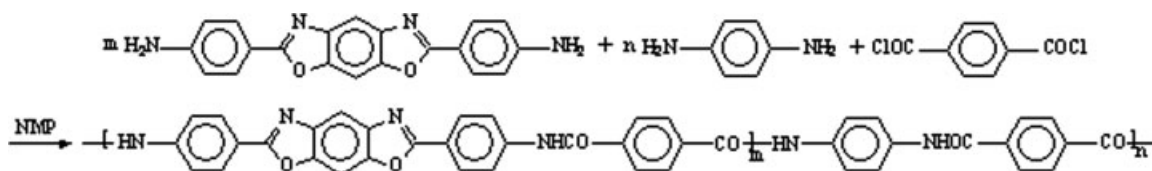
Table I shows results of the copolycondensation at various monomer feed ratios of 2,6-bis(*p*-aminophenyl)benzo[1,2-*d*;4,5-*d'*]bisoxazole for *p*-phenyldiamine. The inherent viscosities of copolymer obtained were increased with increasing *p*-phenyldiamine. Although the maximum η_{nh} was observed at a monomer feed ratio of 10:90 of 2,6-bis(*p*-aminophenyl)benzo[1,2-*d*;4,5-*d'*]bisoxazole:*p*-phenyldiamine. Low inherent viscosity of copolymer containing high ratios of benzobisoxazole was considered due to solubility of the copolymer in solution being poor and copolycondensation being hindered by the gel state of reactive mixture.⁵ To develop molecular weight, reaction mixtures were retained static station in the container for 30 min, and then stirred rapidly. During the synthesis of copolyamide, usual addition mode of diamine to NMP solution was to add 2,6-bis(*p*-aminophenyl)benzo[1,2-*d*;4,5-*d'*]bisoxazole first, followed by one part of terephthaloyl dichloride stirring the reaction solution for 0.5 h, and then *p*-phenyldiamine was added and the solution was stirred for 0.5 h under nitrogen at ambient temperature. This mode of *p*-phenyldiamine addition had little effect upon the inherent viscosities and maintained structure of PPTA unit.

Structure analysis of the homopolymer and copolymers

Figure 3 showed the FTIR spectra of model diamide and homopolyamide. The IR spectrum of model compound was in agreement with that of the corresponding polymer. The latter displayed characteristic absorptions at 3416 (*N*-H str.), 1652 (C=O), 1620 (C=N and aromatic), 1541 (*N*-H deformation), and 1248, 1062 cm^{-1} (C-O-C). Figure 4 showed the ¹H

NMR spectra of homopolyamide, where all the peaks were readily assigned to the aromatic protons of the repeating unit. In ¹H NMR spectrum of model compound and homopolyamide, the resonance for the amino hydrogen disappeared. From analysis of IR and ¹H NMR spectra, the elemental analytic values of the polymers generally agreed well with calculated values for the proposed structures.

The crystallinity of the polyamides was evaluated by wide-angle X-ray diffraction experiments. The typical WAXD patterns of copolyamides containing benzobisoxazole groups, PPTA, and homopolyamide are illustrated in Figure 5(a-e), respectively. In the WAXD patterns of the copolymers containing benzobisoxazole groups [Fig. 5(b-d)], the intensity of reflection peaks from (110) and (200) crystal planes decreased with increasing the 2,6-bis(*p*-aminophenyl)benzo[1,2-*d*;4,5-*d'*]bisoxazole content. The characteristic phenomenon was accompanied by incorporation of the benzobisoxazole units in the crystalline phase. On the other hand, the typical WAXD pattern of homopolyamide was shown in Figure 5(e). It was observed that the homopolyamide displayed three strong reflection peaks around $2\theta = 16.5, 24.06, 26.66$, indicating higher crystallinity. Compared to PPTA [Fig. 5(a)], two strong reflection peaks around $2\theta = 24.06, 26.66$ were undoubtedly assigned to (110) and (200) crystal planes of polyamide section.⁴ The copolymer 40 (contains 40 mol % of 2,6-bis(*p*-aminophenyl)benzo[1,2-*d*;5,4-*d'*]bisoxazole) exhibited an amorphous nature even for polymer derived from rigid 2,6-bis(*p*-aminophenyl)benzo[1,2-*d*;4,5-*d'*]bisoxazole and a medium reflection peaks around $2\theta = 16.5$ which corresponds to benzobisoxazole section of copolyamide. These results could be explained by the presence of the benzobisoxazole group instead of benzen ring inhibited



Scheme 4 Synthesis of copolymer.

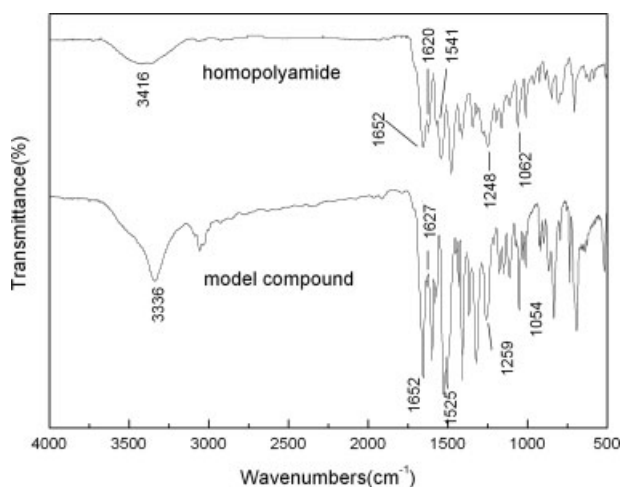


Figure 3 IR spectra of the model compound and homopolyamide.

close-packing of the polymer chains, leading to a decrease in crystallinity.

The crystallinity nature of the polyamides was also reflected in their poor solubility. The aromatic copolyamides showing crystalline patterns were insoluble in polar solvents (such as NMP and DMAC), because the fact that some of them were derived from diamines with a rigid structure, which is in agreement with the general rule that the solubility decreases with increasing crystallinity.

Properties of the homopolymer and copolymers

The thermal stabilities of the copolymers were investigated with TGA in an air stream. Thermogravimetric curves of the copolymers and corresponding homopolymers were compared in Figure 6. In general, all polyamides exhibited good thermal stability. And the onset of decomposition occurred around 500°C in air. Their 10% weight loss temperatures (T_d) were 570–595°C in air, which are reasonable values considering the heterocyclic content of these polymers. Char yields of the copolyamides at 700°C in air were in the range of 52.8–65%, with PPTA having the lowest char yield of 47%, because of the presence of less-rigid diamine moiety. The initial decomposition temperature as well as the temperature at 10% weight loss depended on the copolymer composition and shifted toward high temperature with an increase of the heterocyclic content. The thermal stability was improved dramatically when the copolymer contains small benzobisoxazole units. To analyze the liquid crystalline behavior, the solution of polymer was subjected to polarizing light microscopic analysis. The liquid crystalline behavior of the copolymer was found in the solution of every polymer in 100% H_2SO_4 at 80°C.

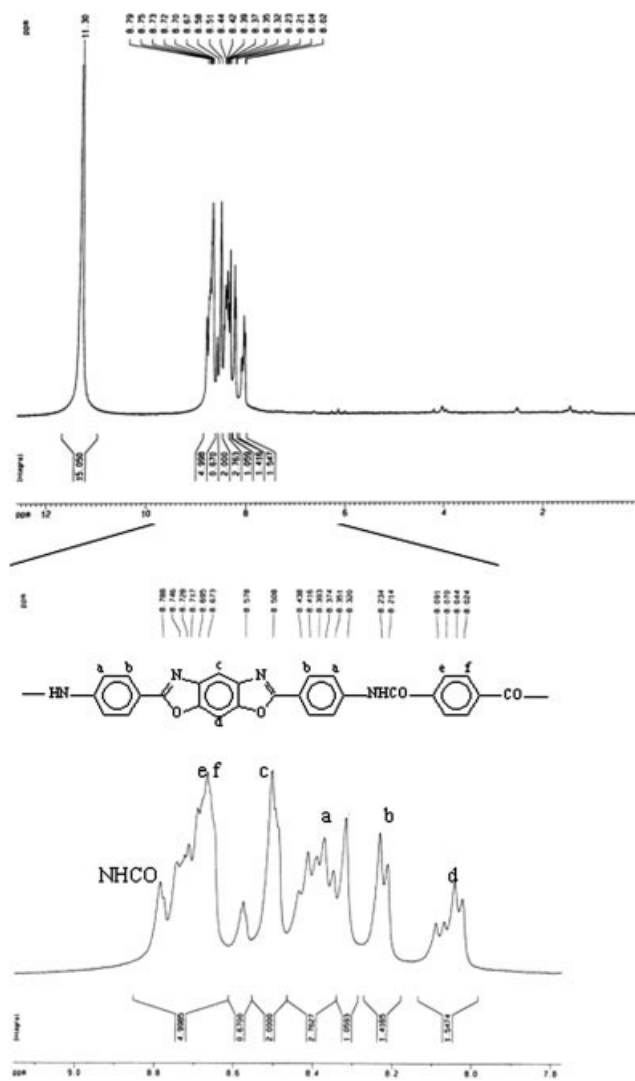


Figure 4 1H NMR spectrum of homopolyamide in CF_3COOD .

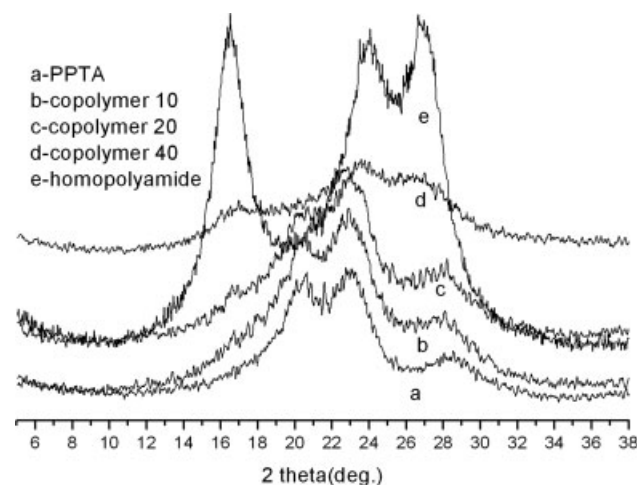


Figure 5 WAXD patterns of PPTA (a), copolymers (b–d), and homopolyamide (e).

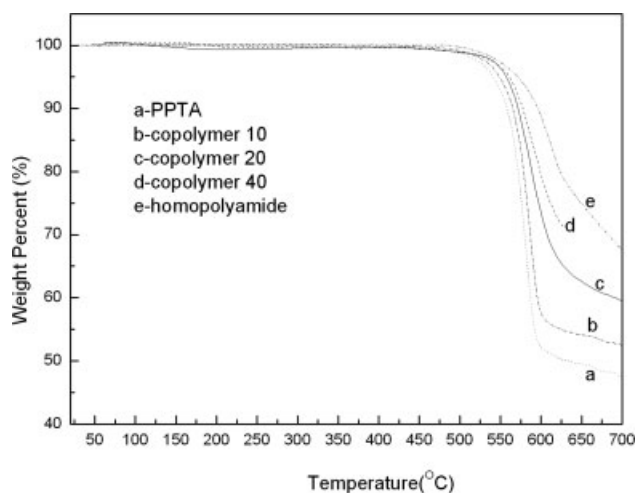


Figure 6 TGA of PPTA (a), copolymers (b–d), and homopolyamide (e).

Structure and properties of the homopolymer and copolymer fibers

The tensile properties of the as-spun fiber were examined. Table I presented the average tensile strength, elongation, and Young's modulus for the polymer fibers containing various concentration of benzobisoxazole, along with thermal property data for polyamides.

Tensile moduli and tensile strength values of fibers from Copolymer 10 were about 33% higher than that of corresponding PPTA fiber. But all were of the same order of magnitude. The tensile moduli and tensile strength values of Copolymer 10 fibers were significantly higher than that of fibers from Copolymer 20 and Copolymer 40, even though molecular weights of all polymers were comparable. Mechanical property of fibers decreased with increase of content of comonomer 2,6-bis(*p*-aminophenyl)benzo[1,2-*d*;5,4-*d'*]bisoxazole. This may originate in comparable limit of crystallinity, degree of orientation, and morphological order. We assumed

that the results in Table I were mainly caused by a different degree of structural disturbance because of the varying content of 2,6-bis(*p*-aminophenyl)benzo[1,2-*d*;5,4-*d'*]bisoxazole. Break extension of copolymer fibers was in general lower than corresponding value for PPTA fiber, but in the same range for all three copolymers.

We focused on the fibers of Copolymer 10 to study the relation of structure and property of polymer fiber. They had an average diameter of 40–45 μm shown in Figure 7. The surface of the filament had many fibrous strips parallel to the fiber axis, because of coagulate process. Structure of the fiber was characterized by X-ray diffraction (XRD) (D8 DISCOVER GADDS of Bruker AXS). And diffraction peak was calculated by multiple peaks separation program. Lattice parameters a , b , c was calculated by using the procedure of lattice parameters calculation. As a result, lattice constant of fiber of Copolymer 10 was $a = 7.980 \text{ \AA}$, $b = 5.084 \text{ \AA}$, $c = 12.928 \text{ \AA}$ and lattice constant of PPTA fiber was $a = 7.910 \text{ \AA}$, $b = 5.202 \text{ \AA}$, $c = 12.901 \text{ \AA}$, $\gamma = 90^\circ$. The lattice constants of PPTA fiber were similar to the value of Kevlar.²⁷ Compared to PPTA fiber, the effect of the introduction of 2,6-bis(*p*-aminophenyl)benzo[1,2-*d*;5,4-*d'*]bisoxazole on the PPTA crystal structure could be described as a quantitative disturbance of the molecular and the supermolecular structure and quantitative structural changed. Intermolecular hydrogen bonding between the O and N of benzobisoxazole ring and the N–H groups of the amide unit lead to the formation of hydrogen bonded sheets within the bc plane.²⁸ Therefore the number of hydrogen bonds increased and thus the b -dimension was also shortened. Meanwhile, the a -dimension was enlarged for steric reason.

CONCLUSIONS

A series of high molecular weight copolyamides were prepared from 2,6-bis(*p*-aminophenyl)benzo

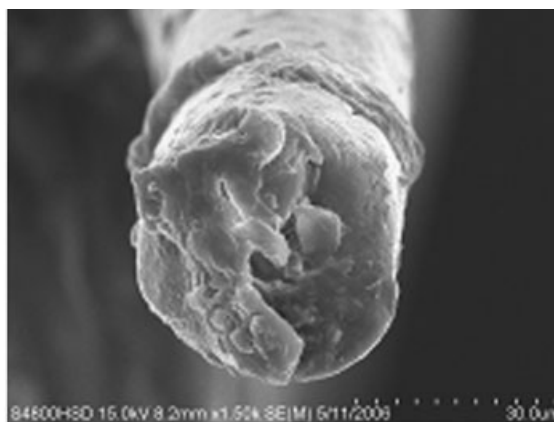
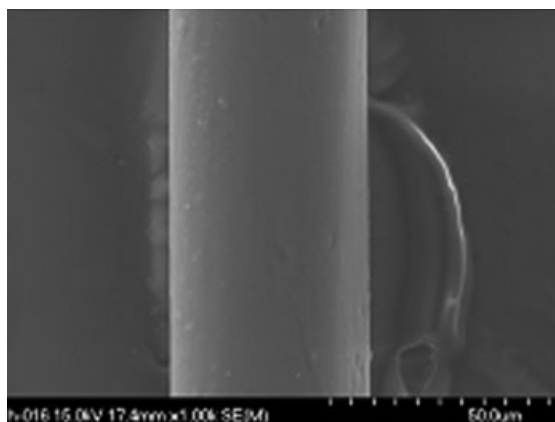


Figure 7 SEM micrographs of surface and fracture surface of the fiber from Copolymer 10.

[1,2-*d*;5,4-*d'*]bisoxazole and *p*-phenylenediamine with terephthaloyl dichloride in high yields. Copolyamides suffered less weight loss than PPTA, and showed excellent thermal stability. In comparison with PPTA, copolyamides showed similar crystallinity and solubility. Compared with PPTA fibers prepared under the same conditions, the tensile strength of copolyamides fibers was improved.

References

1. Penn, L.; Larsen, F. *J Appl Polym Sci* 1979, 23, 59.
2. Fukuda, M.; Kawai, H. *J Polym Sci B: Polym Phys* 1997, 35, 1423.
3. Liaw, D. J.; Liaw, B. Y.; Yang, C. M.; Hsu, P. N.; Hwang, C. Y. *J Polym Sci Part A: Polym Chem* 2001, 39, 1156.
4. Kang, S. J.; Hong, S. I.; Park, C. R. *J Polym Sci Part A: Polym Chem* 2000, 38, 936.
5. Goto, T.; Maeda, M.; Hibi, S. *J Appl Polym Sci* 1989, 37, 867.
6. Müller, W. T.; Ringsdorf, H. *Macromolecules* 1990, 23, 2825.
7. Kricheldorf, H. R.; Schmist, B.; Bürger, R. *Macromolecules* 1992, 25, 5465.
8. Rickert, C.; Neuenschwander, P.; Suter, U. W. *Macromol Chem Phys* 1994, 195, 511.
9. Glomm, B.; Rickert, C.; Neuenschwander, P.; Suter, U. W. *Macromol Chem Phys* 1994, 195, 525.
10. San-José, N.; Gómez-Valdemoro, A.; García, F. C.; Serna, F.; García, J. M. *J Polym Sci Part A: Polym Chem* 2007, 45, 4026.
11. San-José, N.; Gómez-Valdemoro, A.; García, F. C.; de la Peña, J. L.; Serna, F.; García, J. M. *J Polym Sci Part A: Polym Chem* 2007, 45, 5398.
12. Wolfe, J.; Arnold, F. E. *Macromolecules* 1981, 14, 909.
13. Li, J. H.; Chen, X. Q.; Li, X.; Cao, H. L.; Yu, H. Y.; Huang, Y. D. *Polym Int* 2006, 55, 456.
14. Park, K. H.; Kakimoto, M. A.; Imai, Y. *J Polym Sci A: Polym Chem* 1998, 36, 1987.
15. Li, J. H.; Yu, H. Y. *J Polym Sci A: Polym Chem* 2007, 45, 2273.
16. Preston, J.; Cason, J. W. *Polymer* 1993, 34, 830.
17. Harris, W. J.; Hwang, W. F. U.S. Pat. 5,741,585, 1998.
18. Marcos-Fernández, A.; Lozano, A. E.; de Abajo, J.; de la Campa, J. G. *Polymer* 2001, 42, 7933.
19. Kricheldorf, H. R.; Thomsen, S. A. *Makromol Chem Rapid Commun* 1993, 14, 395.
20. Chen, X. Q.; Huang, Y. D.; Li, D. W. *Chin J Org Chem* 2003, 23, 1306.
21. Sato, T.; Cai, Z.; Shiono, T.; Yamamoto, T. *Polymer* 2006, 47, 37.
22. Liou, G. S.; Kakimoto, M. A.; Imai, Y. *J Polym Sci Part A: Polym Chem* 1993, 31, 3265.
23. Yamazaki, N.; Matsumoto, M.; Higashi, F. *J Polym Sci Polym Chem Ed* 1975, 13, 1373.
24. Saverio, R.; Albert, M.; Vladimir, N. I.; Igor, I. P. *Macromolecules* 1993, 26, 4984.
25. Oishi, Y.; Kakimoto, M. A.; Imai, Y. *Macromolecules* 1988, 21, 547.
26. Hsiao, S. H.; Huang, T. L. *J Polym Sci Part A: Polym Chem* 2002, 40, 947.
27. Tashiro, K.; Kobayashi, M.; Tadokoro, H. *Macromolecules* 1977, 10, 413.
28. Rao, Y.; Waddon, A. J.; Farris, R. J. *Polymer* 2001, 42, 5937.