

## Research Article

# Heat and Solvent Resistant Electrospun Polybenzoxazole Nanofibers from Methoxy-Containing Polyaramide

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Polybenzoxazole (PBO) nanofibers were prepared via electrospinning and thermal conversion from its precursor, methoxy-containing polyaramide (MeO-PA). The MeO-PA was synthesized from low-cost monomers. The structures and properties of polymers (MeO-PA and PBO) were characterized by FT-IR, TGA, DSC, OPM, SEM, and so forth. It was found that the PBO nanofibers had a diameter ranging from 300 nm to 350 nm. The PBO nanofiber mats with high porosity provided a promising prospect in high-temperature filter materials, heat insulation materials, and high-temperature protection materials for its outstanding heat and solvent resistance and in preparing carbon nanofibers for its high char yield percentage.

## 1. Introduction

Aromatic polybenzoxazoles (PBOs) are a class of rigid polymers known for super thermal stability and excellent chemical resistance [1, 2]. Traditionally, PBOs have been synthesized via high-temperature polycondensation with 4, 6-diamino-resorcinol dihydrochloride (DAR·2HCl) and terephthalic acid or its derivatives in polyphosphoric acid (PPA) or methanesulfonic acid (MSA) [3–7]. This method involved complex monomer synthesis and purification procedures. Moreover, it is difficult to remove residual solvent MSA which was embedded in the polymers, which limited the large-scale production and application of PBOs [1, 4, 8, 9].

Using a dry-jet wet-spinning process, commercial PBO crude fibers with a diameter about 10–15  $\mu\text{m}$  were obtained [4, 7]. However, PBO nanofibers with a diameter in the range of several hundreds nanometers were rarely reported. For the small diameter, large specific surface area, and excellent adsorption properties, nanofibers have been widely used in biomedical materials, high-temperature filters and separator materials, and high-temperature protection materials [10–14]. In the last 1990s, PBO nanofibers prepared by electrospinning were mentioned by Reneker and chun [11], but there was no further report. The reason might be that PBO

was only soluble in strong acid but was insoluble in common organic solvents. This made PBO unfavorable to directly electrospin.

In recent years, two-step thermal conversion of PBO from precursors, *o*-hydroxy polyamide or polyimide, which were synthesized by *o*-hydroxy aromatic diamine and aromatic dianhydride or aromatic diacid chloride, had become popular [15–17]. This method provided a simple, available, and feasible way to obtain PBO nanofiber by electrospinning soluble precursors of PBO. However, the monomers of *o*-hydroxy aromatic diamines are difficult to synthesize and led to high price, which limited the mass production of electrospun PBO nanofibers. Some previous works indicated that PBO can be also prepared via polycondensation and thermal conversion from much cheaper monomers of *o*-methoxy aromatic diamine and aromatic dianhydride or aromatic diacid chloride [18, 19]. In this study, low-price monomers of 4, 4'-diamino-3, 3'-dimethoxydiphenyl (DMOBPA), and isophthaloyl dichloride (IPC) were selected to synthesize PBO precursors, methoxy-containing polyaramide (MeO-PA) solution. The as-synthesized MeO-PA was electrospun into nanofibers and subsequently thermally converted into PBO nanofibers. This method offers a bright prospect for large-scale production of heat and solvent resistant PBO nanofibers.

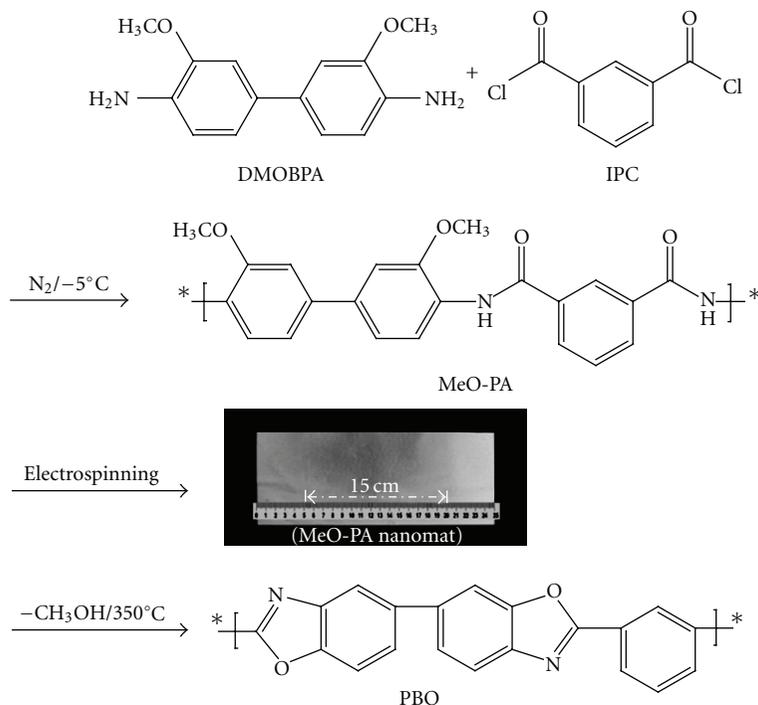


FIGURE 1: A schematic diagram for the preparation of electrospun PBO nanofibers.

## 2. Experimental

**2.1. Materials and Measurements.** IPC was purchased from Jiangxi Lianda Chemical Co., China. DMOBPA was obtained from Shanxi Beichen Daily chemical limited Co., Ltd., China. Pyridine and anhydrous lithium chloride (LiCl) were respectively supplied by Jiangsu Qiangsheng Chemical Co., China and Guangdong Shantou Xilong Chemical Co., China. *N,N'*-Dimethylacetamide (DMAC) was obtained from Shanghai Jingwei Chemical Co., China. IPC and DMOBPA were both purified by sublimation before use. Pyridine and DMAC were distilled under vacuum distillation, while other reagents were used as received.

Inherent viscosity was measured with Ubbelohde viscometer (Shanghai SRD Sci. Instrument Co.) on DMAC solutions of 0.5 g/dL at  $25^{\circ}\text{C}$ . Fourier transform infrared (FT-IR) spectrum was recorded on a Bruker tensor 27 spectrophotometer in the range of  $4000\text{--}400\text{ cm}^{-1}$ . Thermal Gravimetric Analysis (TGA) was carried out on a thermogravimetric analyzer WRT-3P (Shanghai) at a scan rate of  $10^{\circ}\text{C}/\text{min}$  in flowing  $\text{N}_2$  (80 ml/min). Differential Scanning Calorimetry (DSC) curves were obtained by NETZCH-DSC 200F3 at a heating rate of  $10^{\circ}\text{C}/\text{min}$  under  $\text{N}_2$ . The pictures of MeO-PA nanomat and morphology micrographs of polymer nanofibers were taken by an Olympus FE-250 camera (8.0 mega pixels/image), a Quanta 200 scanning electron microscope (SEM), and polarizing microscope (POM) Nikon eclipse E200, respectively.

**2.2. Synthesis and Fabrication of MeO-PA Nanofibers.** MeO-PA solution for electrospinning was prepared by polycondensation of DMOBPA and IPC in DMAC solution in

the presence of pyridine and LiCl at  $-5^{\circ}\text{C}$  for 2 hr [18], yielding a 20 wt% pale yellow transparent MeO-PA solution. The inherent viscosity of the resultant MeO-PA solution was 1.20 dL/g measured at a concentration of 0.50 g/dl at  $25^{\circ}\text{C}$ .

The above MeO-PA solution was diluted to a concentration of 15 wt% by DMAC for electrospinning, using an apparatus equipped with an electric field of 100 kV/m, applying a 30 kV electrical potential to a 30 cm gap between a spinneret and a metal mesh collector, at a feeding rate of 0.8 ml/h, resulting in a  $25\text{ cm} \times 10\text{ cm}$  nanofiber non-woven mat. The mat was extracted in a Soxhlet with a mixed solvent of distilled water and anhydrous methanol for 48 hr to remove the salt LiCl, pyridinium, and the solvent DMAC and then dried in a vacuum oven at  $100^{\circ}\text{C}$  for 4 hr to remove the residual solvent. Then, the resulting mat with thickness of  $25\text{ }\mu\text{m}$  was treated at  $200^{\circ}\text{C}$ ,  $330^{\circ}\text{C}$ , and  $350^{\circ}\text{C}$  under  $\text{N}_2$  atmosphere and annealed for about 2 hr at each step. Figure 1 showed the preparation of electrospun PBO nanofibers and a photograph of MeO-PA nanomat.

## 3. Results and Discussion

**3.1. Thermal Conversion of MeO-PA Nanomats.** The thermal conversion from MeO-PA nanofiber mat to PBO was investigated via IR spectra, thermogravimetric analysis (TGA), and differential scanning calorimetry (DSC). Figure 2 shows typical FT-IR spectra of MeO-PA treated at different temperatures. The FT-IR spectrum of MeO-PA heated at  $200^{\circ}\text{C}$  for 2 hr was found to be almost the same as that of MeO-PA at  $100^{\circ}\text{C}$ . The absorptions at  $3422\text{ cm}^{-1}$  (N-H, stretching),

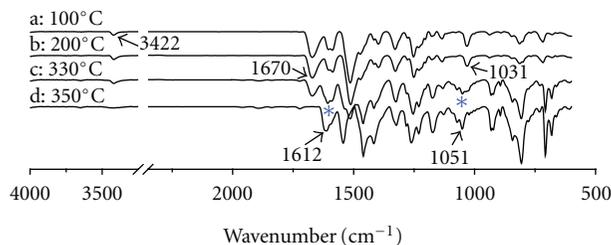


FIGURE 2: FT-IR spectra of MeO-PA with different treating temperatures.

1670  $\text{cm}^{-1}$  (C=O, stretching), 1598  $\text{cm}^{-1}$  (N-H, bending, C-N, stretching), and 1031  $\text{cm}^{-1}$  (Ar-O-CH<sub>3</sub>, stretching) still remained, and no sign of benzoxazole ring could be found at all, which indicated that the thermal conversion of PBO did not occur when the PA mat was heated to 200°C. As the temperature increased to 350°C, absorption peaks at 1612  $\text{cm}^{-1}$  (\*) and 1051  $\text{cm}^{-1}$  (\*) gradually increased, which provided an evidence of the formation of polybenzoxazole ring [15–17]. The thermal conversion from MeO-PA mat to PBO was carried out completely at 350°C, as proven by the disappearance of characteristic amide carbonyl peaks at 1670  $\text{cm}^{-1}$ , 3422  $\text{cm}^{-1}$  (N-H, stretching), 1600  $\text{cm}^{-1}$ , and 1031  $\text{cm}^{-1}$  and the appearance of characteristic benzoxazole ring absorptions at 1612  $\text{cm}^{-1}$ , 1051  $\text{cm}^{-1}$ , which confirmed that the amide group reacted with the methoxyl group and formed benzoxazole ring.

The TGA curves of MeO-PA samples treated at 200°C and 350°C provided additional information about the thermal conversion of MeO-PA mat as shown in Figure 3. TGA trace of MeO-PA (200°C) revealed two distinct weight-loss steps of thermal conversion. The first step, occurring between about 250°C and 420°C, was attributed to the intramolecular cyclization of the neighboring groups of -OCH<sub>3</sub> and -NHCO- on the benzene ring to form oxazole ring and corresponded to a weight loss of 21.5%, which matched up the theoretical mass loss occurring upon the loss of 2 mol of CH<sub>3</sub>OH per unit of 20.31%. The second step, started at about 600°C, could be attributed to the decomposition of PBO. DSC trace (Figure 4) of MeO-PA (a) exhibited a strong exothermic process from 300°C and 400°C that was attributed to the loss of CH<sub>3</sub>OH during the formation of oxazole ring, whereas no significant heat changes in another trace of sample (b) implied a completely conversion to PBO when MeO-PA mat were heated at 350°C for 2 hr.

The above results from FT-IR, TGA, and DSC curves were correspondent with each other and provided clear evidence that the MeO-PA mat was converted to PBO when heated at 350°C, which was 150°C lower than the converting temperature of hydroxyl- or methoxy-containing polyimide [15, 17, 19].

**3.2. Morphology of Polymer Nanofibers.** MeO-PA nanofibers were prepared by electrospinning of a 15 wt% solution of MeO-PA and collected onto a metal mesh, imposing a 30 kV electrical potential at a feeding rate of 0.8 ml/h.

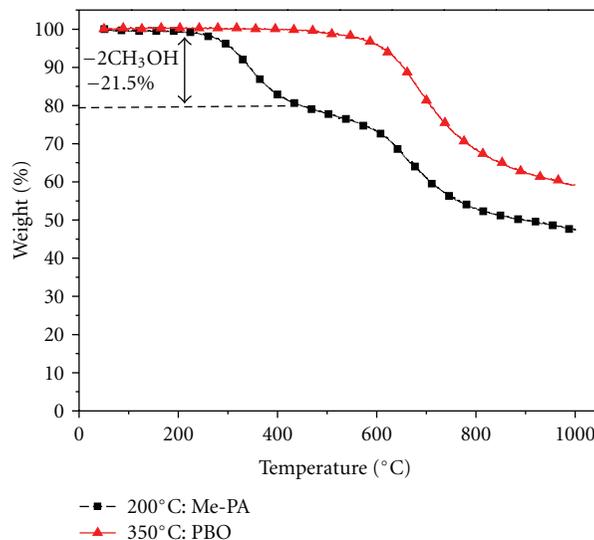


FIGURE 3: TGA curves of MeO-PA treated at 200°C and 350°C at a heating rate of 10°C/min in N<sub>2</sub>.

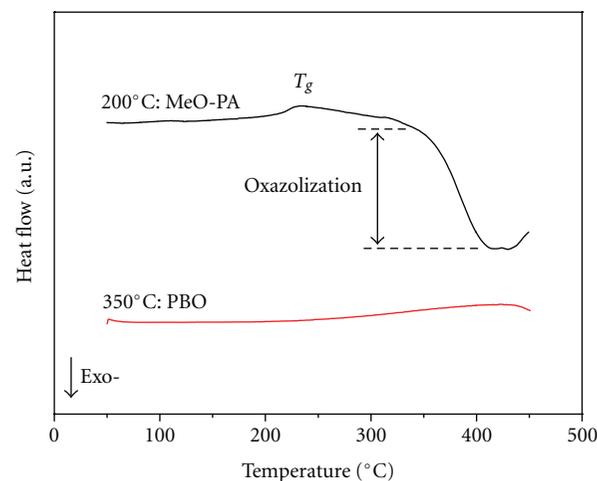


FIGURE 4: DSC curves of MeO-PA treated at 200°C and 350°C at a heating rate of 10°C/min in N<sub>2</sub>.

PBO nanofibers were obtained by heating treatment of MeO-PA nanofibers at 350°C for 2 hr. The SEM images of collected nanofibers are shown in Figure 5. Fibers were uniform with a centralized diameter distribution of 300–350 nm in images (a), (b) and (c), (d). More coiled fibers stacking could be seen in (a) than in (c) because MeO-PA has more flexible molecule configuration than that of the rigid rod-like benzoxazole molecule. What is more, the nanopores with a size distribution of several nanometers to several micrometers were formed both in MeO-PA and PBO nanomats by electrospinning, which was favorable to fabricate microfiltration or nanofiltration materials [20].

**3.3. Thermal Properties of Polymer Nanofiber Mats.** The thermal properties of MeO-PA and PBO nanomats in N<sub>2</sub> atmosphere were characterized by TGA and DSC.

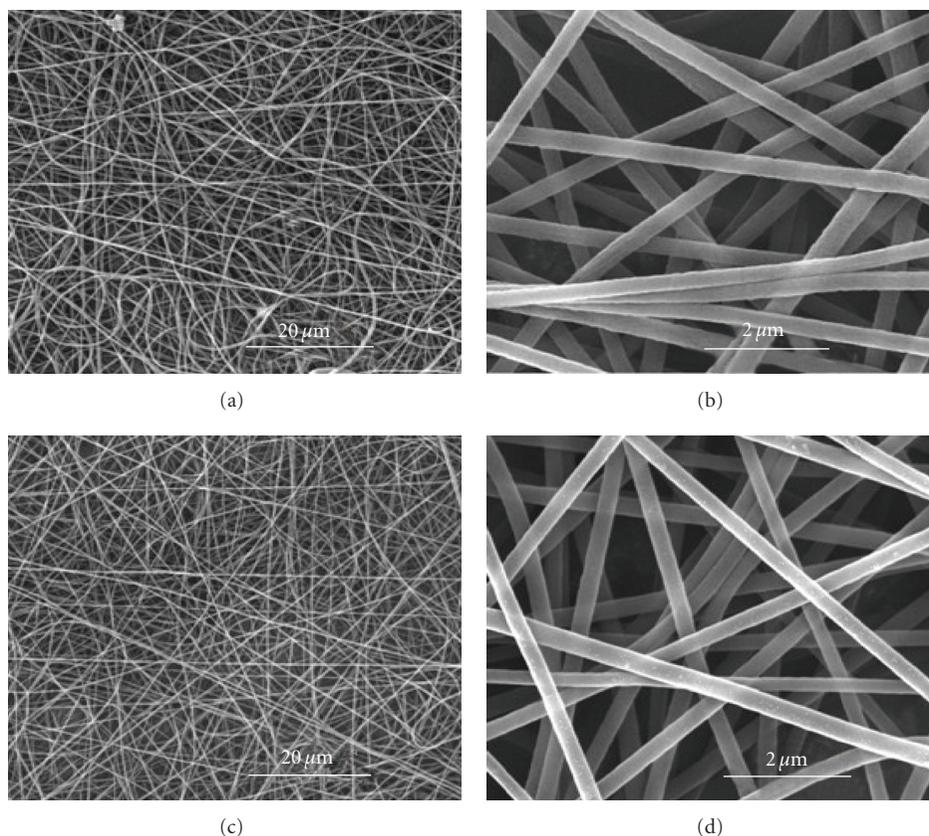


FIGURE 5: SEM images of polymer nanofibers. (a) and (b): MeO-PA nanofibers; (c) and (d): PBO nanofibers.

TABLE 1: Prices comparison of *o*-hydroxy aromatic diamines and DMOBPA.

Name abbr.	CSA number	Company	Purity	Price (\$/25 g)
IPC	99-63-8	TCI	99.0%	26.0
DAR-2HCl	16523-31-2	TCI	98.0%	483.8
DHB	2373-98-0	TCI	98.0%	366.2
BisAPAF	83558-87-6	TCI	98.0%	270.6
DMOBPA	119-90-4	Alfa Aesar	98.0%	105.9
		TCI	95.0%	42.01

As shown in Figure 3, TGA curves of MeO-PA nanofiber mat revealed that weight loss started around 200°C due to the thermal conversion while that of PBO nanomat exhibited firstly decomposition around 500°C for the stable and rigid rod-like molecule structure. The 5% weight-loss temperature ( $T_5$ ), 10% weight-loss temperature ( $T_{10}$ ), and char yield percentage at 1000°C of MeO-PA and PBO are summarized in Table 2. The  $T_5$  and  $T_{10}$  values of PBO were 611°C and 654°C, respectively, which were higher than that of *i*-BPDA-MPD-PI with similar molecule structure [21]. This clearly indicates that the thermal stability of PBO nanofiber mat in an inert nitrogen atmosphere was much higher than that of PIs. In addition, the char yield of PBO nanofiber mat was as high as 59.3% at 1000°C, which was even higher than the char yield of PMDA-DMB-PI

TABLE 2: Thermal properties of different polymers.

Sample	$T_g^a$ (°C)	$T_{5\%}^b$ (°C)	$T_{10\%}^b$ (°C)	Char yield <sup>c</sup> (%)
MeO-PA nanomat	228	305	342	47.6 <sup>c</sup>
PBO nanomat	ND	611	654	59.3 <sup>c</sup>
<i>i</i> -BPDA-MPD-PI <sup>21</sup>	—	552	—	—
PMDA-DMB-PI <sup>22</sup>	341.6	500	581	51.0 <sup>d</sup>

<sup>a</sup>: Glass transition temperature detected by DSC; ND: none detected;

<sup>b</sup>: 5% and 10% weight loss temperature recorded by TGA;

<sup>c</sup>: char yield percentage (%) at 1000°C in N<sub>2</sub>;

<sup>d</sup>: char yield (%) at 800°C in N<sub>2</sub>.

at 800°C [22]. Therefore, this kind of PBO nanofiber mat might become a prospective precursor material for carbon nanofibers.

**3.4. Solubility Properties of Polymer Nanofiber Mats.** The solubility behavior of MeO-PA and PBO nanofiber mats was tested in different kinds of solvents, and the results are summarized in Table 3. MeO-PA nanomats were soluble in CSA, MSA, DMAc, and DMF with addition of LiCl, soluble in DMSO and NMP while heating, while insoluble in nonpolar solvents, such as ethyl ether, chloroform. But, PBO nanomats showed an excellent solvent-resistant property. Except for strong acids, such as MSA and CSA, PBO nanomats were insoluble in any organic solvents due to the existence of rigid rod-like segment in polymer backbones.

TABLE 3: Solubility behavior of MeO-PA and PBO nanomats.

Sample	DMAc	DMF	CSA	DMSO	MSA	Ethyl ether	Chloroform	NMP
MeO-PA	+-	+-	++	+h	++	--	--	+h
PBO	--	--	++	--	++	--	--	--

++: soluble at room temperature; +h: soluble on heating; +-: soluble by adding LiCl; --: insoluble; CSA: concentrated sulfuric acid; MSA: methanesulfonic acid.

#### 4. Conclusions

PBO nanomats were prepared from monomers DMOBPA and IPC by polycondensation, electrospinning, and thermal conversion. The PBO nanofiber had diameter ranging from 300 nm to 350 nm. The resulting PBO nanomat with an initial decomposition temperature of 500°C and 5% weight loss temperature up to 611°C contained many nanopores with a size distribution of several nanometers to several micrometers, and it was quite insoluble in organic solvents. Due to the use of low-cost monomers, electrospun PBO nanofiber mats by this method provided a bright prospect for large-scale production of heat and solvent resistant PBO nanofibers.

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