

Research Article

Synthesis and Preliminary Properties of Novel Poly(aryl ether)s Containing β -Naphthalene Pendant Group

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Two novel poly(aryl ether)s containing β -naphthalene pendant group were synthesized and the structures of these polymers were confirmed by ^1H NMR spectroscopy. The polymers exhibited good thermal stabilities with high T_g of 256°C and 274°C, respectively. The polymers are soluble in common organic solvents, such as DMAc, DMSO, CH_2Cl_2 , and CHCl_3 , and can be electrospun into microfiber (1–5 μm) with lots of nanopores (<100 nm) from CHCl_3 solution. These fibers showed high hydrophobicity, and the contact angle of fibers is above 120°.

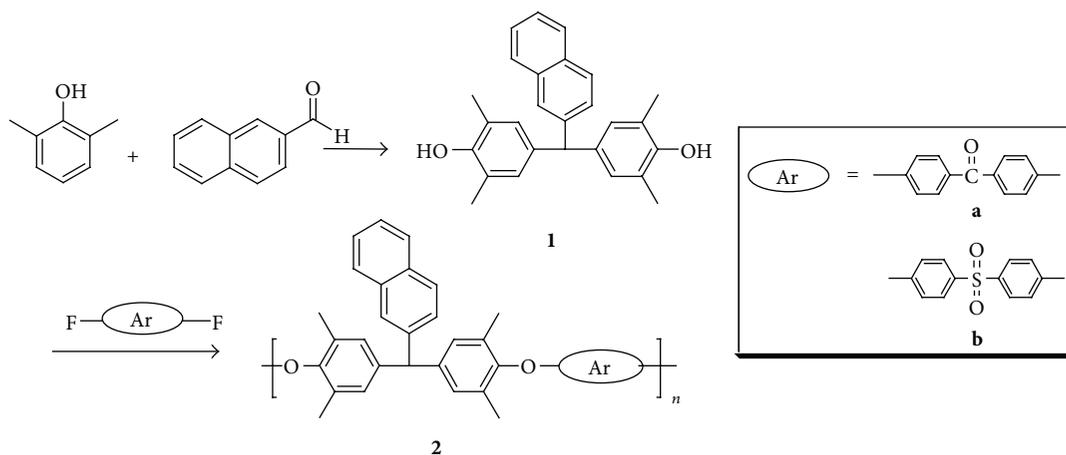
1. Introduction

Poly(aryl ether)s [1–10] have extensive applications in aerospace, aviation, electronics, telecommunications, nuclear energy, and other high technology fields because of their excellent properties, such as heat resistance, radiation resistance, impact resistance, and chemical resistance. Poly(aryl ether ketone)s (PAEKs) and poly(aryl ether sulfone)s (PAESs) are two important commercial poly(aryl ether)s. It is difficult for the standard PAEKs to be used as thin films and coating materials because of their semicrystalline property and poor solubility. For PAESs, their solvent resistance is often poor and they could not form oriented film or fiber [11, 12]. Therefore, study on improving the processing properties and solubility of poly(aryl ether)s through structural modification is one of the research hotspots. Structure changes have focused on the introduction of semi flexible groups (such as sulfone, sulfur ether, methylene substituents) to improve the solubility and rigid groups (such as naphthalene [12–14], aromatic heterocyclic, anthracene) to enhance the thermal stabilities, and the incorporation of pendant alkyl or phenyl groups on to the poly(aryl ether) in the backbone of the polymeric chain [15–19]. Our group has synthesized and characterized poly(aryl ether)s with pendant α -naphthyl groups [20]. Recent study indicated that these polymers

could be electrospun into microfiber with nanopores [12]. As we know that the properties of compounds substituted with α -naphthalene and β -naphthalene are different, we think that if β -naphthyl groups are introduced into the poly(aryl ether) chain, the properties of the polymers may be enhanced. In order to further study poly(aryl ether)s with pendant naphthyl groups, two novel poly(aryl ether)s were synthesized by using bis(3,5-dimethyl-4-hydroxyphenyl)- β -naphthyl methane and 4,4'-difluorobenzophenone or bis(4-fluorophenyl) sulfone through nucleophilic aromatic substitution. The thermal stabilities and solubility were investigated. In addition, these polymers could be made into fibers and the morphologies of the fibers were also characterized.

2. Experimental Section

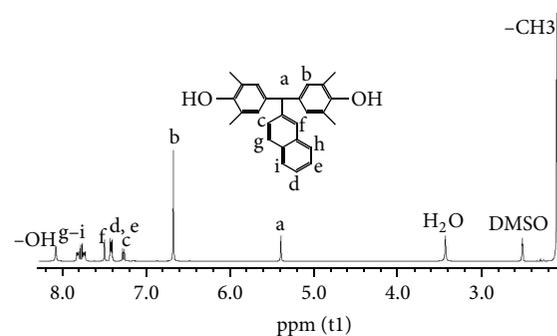
2.1. Materials. Bis(3,5-dimethyl-4-hydroxyphenyl)- β -naphthyl methane, 4,4'-difluorobenzophenone, bis(4-fluorophenyl) sulfone, 3-mercaptopropionic acid, and sulfuric acid (60%) were purchased from commercial sources and used as received. Toluene was dried with sodium wire and DMAc was dried with 4 Å molecule sieves prior to use. Anhydrous potassium carbonate was dried at 300°C for 24 h in furnace prior to use.

SCHEME 1: Syntheses of monomer **1** and polymers **2**.

2.2. Characterization and Methods. $^1\text{H-NMR}$ spectra, reported in ppm, were recorded on a Varian 400 Hz NMR instrument using DMSO-d_6 or chloroform as the solvent and tetramethylsilane (TMS) as the internal standard. The thermal stability of the polymers was evaluated on a Perkin-Elmer TGA/DTA 6300 at a heating rate of $20^\circ\text{C}/\text{min}$ under nitrogen. A Perkin-Elmer DSC-7C calorimeter was used to measure the T_g at a heating rate of $20^\circ\text{C}/\text{min}$ under nitrogen. The average molecular weights of the polymers were estimated by a Waters 510 HPLC gel permeation chromatography (GPC) system equipped with $5\ \mu\text{m}$ phenol gel columns (linear, $4 \times 500\ \text{\AA}$) arranged in series using polystyrene as the standard. Microscopic surface morphology of polymer fiber was studied with a JEOL JSM-5610 scanning electron microscope (SEM). Water contact angles of the polymer films on a glass slide were measured with a 59980-35 contact angle analyzer from COLE-PARMER. Melting points were taken on a XT4A melting point apparatus.

2.3. Syntheses of Monomer 1 and Polymers 2. As depicted in Scheme 1, bis(3,5-dimethyl-4-hydroxyphenyl)-2-naphthyl methane (monomer **1**) was synthesized. To a 100 mL three-neck round bottom flask, equipped with a reflux condenser, magnetic stirrer, nitrogen inlet, and a drop funnel, 2-naphthaldehyde (15.6 g, 0.1 mol), 2,6-dimethylphenol (36.6 g, 0.3 mol), 40 mL of toluene were introduced. A portion of 10 mL of 60 wt% H_2SO_4 with 5 drops of 3-mercaptopropionic acid was added dropwise at room temperature for 30 min. The reaction mixture was heated at $50\text{--}55^\circ\text{C}$, stirring for 12 h, until the viscous pink precipitation was produced. The resulting mixture was washed with water 3 times and small amount of toluene 2 times and then recrystallized with toluene 2 times. Finally, we get light-yellow crystal. After filtration, the precipitation was dried at 30°C under vacuum for 24 h. Melting point (T_m) was $166\text{--}167^\circ\text{C}$.

The structure of the monomer was confirmed by $^1\text{H-NMR}$ spectra (Figure 1). $^1\text{HNMR}$ (DMSO-d_6 , δppm): 2.102 (s, 12H), 5.399 (s, 1H), 6.688 (s, 4H), 7.295–7.299 (d, 1H), 7.446–7.512 (m, 3H), 7.743–7.845 (m, 3H), 8.097 (s, 2H). Elemental

FIGURE 1: $^1\text{H-NMR}$ spectrum of monomer **1** in DMSO-d_6 .

analysis: calculated for $\text{C}_{27}\text{H}_{26}\text{O}_2$ (382.49): C, 84.78; H, 6.85. Found: C, 84.67; H, 6.80.

The poly(aryl ether)s were prepared as depicted in Scheme 1. To a 25 mL three-neck round bottom flask equipped with a part flow arrangement and condenser under nitrogen, 4,4'-difluorobenzophenone (0.218 g, 1.0 mmol) or bis(4-fluorophenyl) sulfone (0.254 g, 1.0 mmol), bisphenol monomer **1** (0.382 g, 1.0 mmol), anhydrous potassium carbonate (0.208 g, 1.5 mmol), DMAc (2.0 mL), and toluene (5 mL) were carefully introduced. The reaction mixture was first heated at $140\text{--}150^\circ\text{C}$ for 4 h to remove the water produced by azeotropic distillation. Then the temperature was increased to $170\text{--}180^\circ\text{C}$ and this temperature was kept for 2–3 h. After it was cooled, the resulting mixture was diluted with 2 mL DMAc and poured into 100 mL methanol containing 2 mL of concentrated HCl slowly to precipitate white nodular solid. The white solid polymer was washed with methanol. After drying, the polymer was dissolved in 50 mL chloroform and filtered through a funnel. The filtrate was concentrated to about 7 mL and then added dropwise into 100 mL methanol to precipitate out the white polymer. After filtration, the precipitation was dried at 120°C under vacuum for 24 h (yield: 92%).

The structure of the polymers was confirmed by $^1\text{HNMR}$ spectra (Figure 2). $^1\text{HNMR}$ (CDCl_3 , δppm): polymer **2a**:

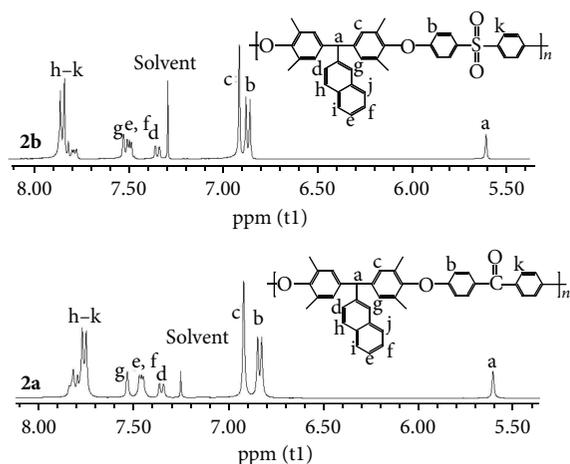


FIGURE 2: ^1H NMR spectrum of polymers **2** in CDCl_3 .

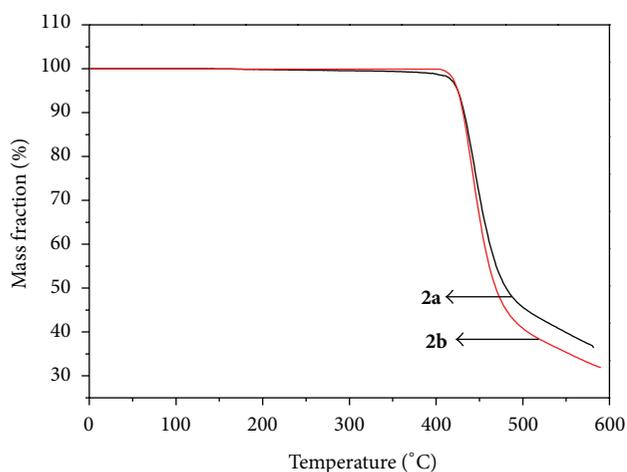


FIGURE 3: TGA curves of polymers **2**.

2.080 (s, 12H), 5.608 (s, 1H), 6.824–6.845 (m, 4H), 6.919 (s, 4H), 7.341–7.362 (d, 1H), 7.446–7.467 (m, 2H), 7.531 (s, 1H), 7.746–7.768 (m, 5H), 7.814 (m, 2H); polymer **2b**: 2.007 (s, 12H), 5.575 (s, 1H), 6.823–6.845 (m, 4H), 6.880 (s, 4H), 7.300–7.325 (d, 1H), 7.449–7.491 (m, 3H), 7.740–7.783 (m, 5H), 7.902–7.907 (m, 2H).

2.4. Electrospinning Setup. The condition of electrospinning at the room temperature was illustrated as follows: the polymers were dissolved in CHCl_3 with a dissolvability of 7.5 wt% (polymer **2a**) and 6 wt% (polymer **2b**), respectively. The solutions were placed in a syringe with metallic needle (inner tip diameter of 1 mm) and a grounded aluminum sheet (thickness, 0.02 mm) was used as the collector. The distance between the spinneret and collector plate was 15 cm. The voltage was 30 kV. The ejection rate of the solution was 5 mL/h. The distance between the tip of the syringe (anode) and the surface of collector (cathode) was 15 cm. The applied direct current voltage was 30 kV. The ejection rate

TABLE 1: Molecular weights and thermal properties of polymers.

Polymer	M_n ($\times 10^4$)	M_w ($\times 10^4$)	T_g ($^\circ\text{C}$)	$T_{5\%}$ ($^\circ\text{C}$)
Polymer 2a	8.7	16.2	256	418
Polymer 2b	7.8	13.5	274	424
α -Polymer a [20]	9.6	24.4	252	417
α -Polymer b [20]	8.9	24.3	273	447

of the solution from the syringe was kept at 5 mL/h and the electrospinning process was carried out in air.

3. Results and Discussion

3.1. Thermal Properties and Hydrophobicity. Thermal properties of the polymers were given in Table 1 and Figure 3. The polymers exhibited excellent thermal properties with 5% mass loss at $T > 400^\circ\text{C}$ and high T_g of $T > 250^\circ\text{C}$. Compared to the results of the polymers containing α -naphthalene groups [20], the T_g slightly raised due to the introduction of β -naphthalene group. With the introduction of bulky β -naphthalene group in the polymer side chain, the chain segment movement steric hindrance increased, so that the T_g of the polymer containing β -naphthalene group increased. The T_g of the polymer **2b** is significantly higher than that of polymer **2a** due to the introduction of the sulfone group. Similar with the polymers containing α -naphthalene groups, the polymers containing β -naphthalene group failed to show the melting points. This indicated they were amorphous in nature. The WAXD spectra showed a diffuse scattering peak from 12° to 25° with no crystallization peak and further confirmed the amorphous nature.

The contact angles both for water and glycerol on polymer films and fiber membranes were measured. The contact angles on both of the fiber membranes were about 120° (part of the contact angles were shown in Figure 4), however, on the films only around 90° . It indicated that the hydrophobicity of poly(aryl ether)s was improved by electrospinning, because the surface free energy of fibers was much higher than that of films.

3.2. Solubility and Morphology. The polymers were soluble in common organic solvents, such as CHCl_3 , CH_2Cl_2 , THF, DMAc, and DMSO, and could be electrospun into microfiber with lots of nanopores. The scanning electron micrographs of polymers **2a** and **2b** fibers were shown in Figures 5 and 6, respectively.

The SEM of the polymer fibers showed that the fibers were all ribbon-shaped, and the average diameters of polymers **2a** and **2b** fibers were about $1\ \mu\text{m}$ and $5\ \mu\text{m}$, respectively. These poly(aryl ether) fibers are not solid; there are a lot of pores, even the fibers are hollow. Moreover, there were lots of nanopores on the poly(aryl ether) fibers, and many nanopores are communicated with the internal. The nanopores were probably produced by the rapid evaporation of chloroform solvent.

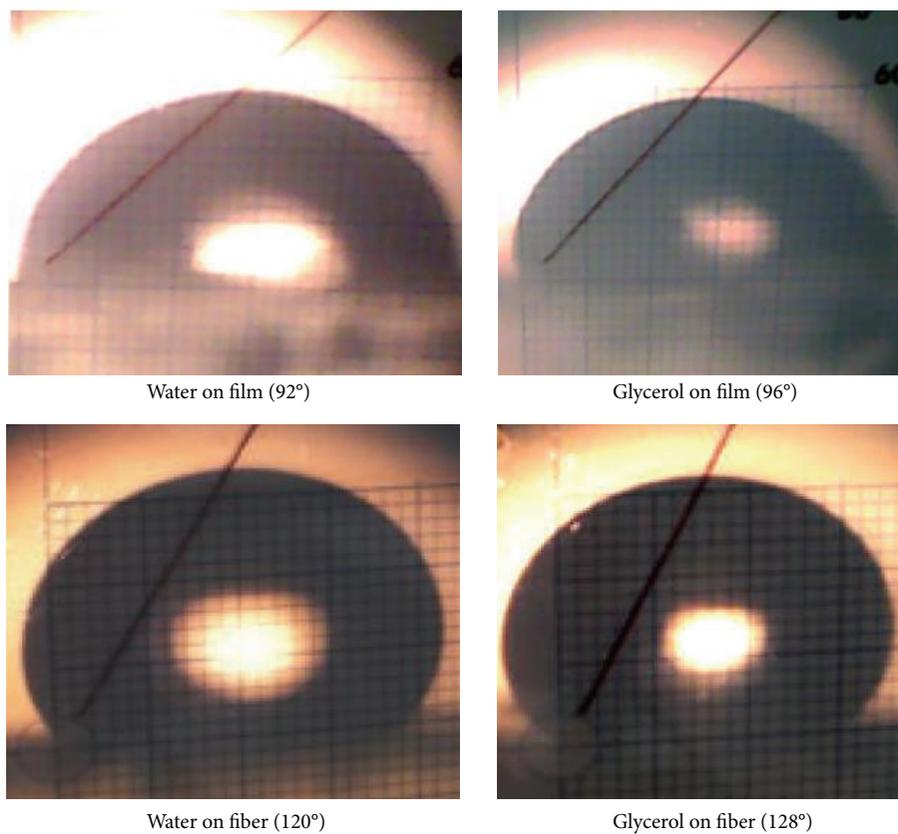


FIGURE 4: The profiles of a droplet on the polymer **2a** surface.

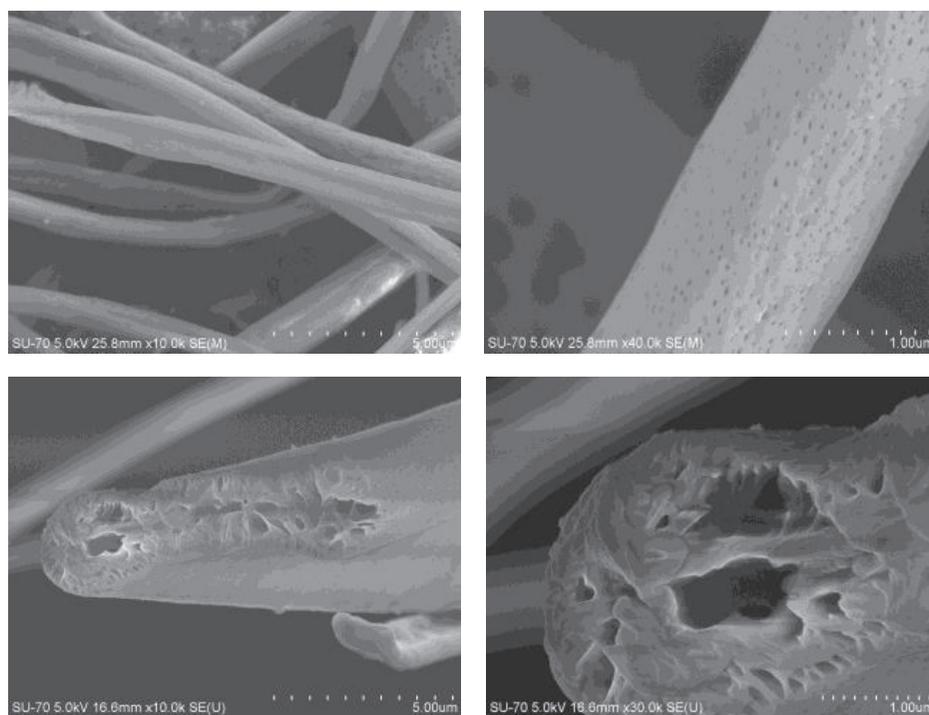


FIGURE 5: Scanning electron micrographs of polymer **2a** fiber.

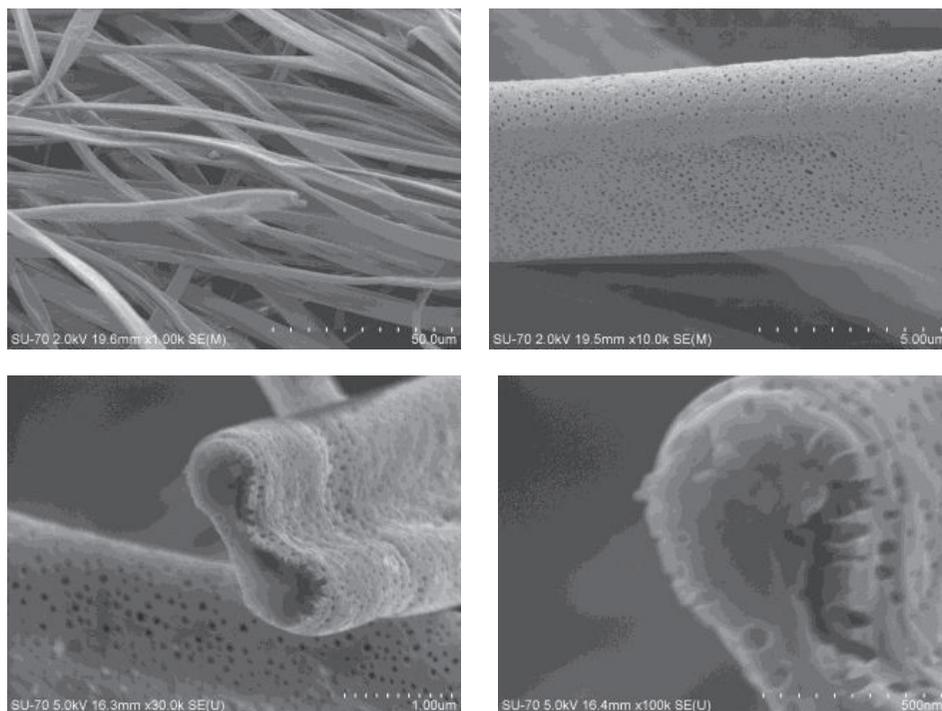


FIGURE 6: Scanning electron micrographs of polymer **2b** fiber.

4. Conclusion

The novel poly(aryl ether)s containing β -naphthalene pendant group were successfully synthesized. These polymers had excellent thermal stabilities and good solubility. The fibers with many nanopores that were produced by electrospinning exhibited high hydrophobicity. The polymers could be potentially used as high temperature materials, waterproof materials, and transport carriers.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

Acknowledgments

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