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Crosslinkable fully aromatic poly(aryl ether ketone)s bearing macrocycle of aryl ether ketone

Xigui Yue, Haibo Zhang, Wenhui Chen, Yishan Wang, Shuling Zhang, Guibin Wang, Zhenhua Jiang*

Alan G. MacDiarmid Lab, College of Chemistry, Jilin University, Xiuzheng Road 1788, Changchun, Jilin 130023, People's Republic of China

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Abstract

A novel bisphenol monomer, (3-methoxy)phenylhydroquinone, was synthesized via a three-step synthetic procedure. The cyclization of the bisphenol monomer and 4,4-difluorobenzophenone was carried out under pseudo high dilution condition. Two types of fully aromatic poly(aryl ether ketone)s were prepared by copolymerization of macrocycle of aryl ether ketone (MACEK) containing hydroxyphenyl, 4,4′-(hexafluoroisopropylidene)diphenol (HFBPA), and 4,4-difluorobenzophenone. The copolymers have high molecular mass, good solubility and high glass transition temperatures. The copolymers are crosslinkable in the presence of basic initiator and the glass transition temperatures of the copolymers increased greatly after the curing. These cured copolymers exhibit excellent thermal stability, and the 5% weight loss temperatures are around 500 °C in nitrogen.

Keywords: Macrocycle; Poly(aryl ether ketone) copolymer; Crosslinking

1. Introduction

Poly(arylene ether ketone)s (PAEKs), which are well-known high performance polymers used in a wide range of demanding applications from aerospace to microelectronics, are characterized by their excellent thermal, mechanical, and environmental stabilities [1–3]. A nonsubstituted PAEKs show highly crystalline properties, resulting in its very low solubility toward common organic solvents, although the crystallinity maintains the better mechanical and thermal properties. Because of their poor solubility, it is difficult for conventional PAEKs to be applied as thin films and coating materials. In addition, their poor solubility makes the polymerization conditions rigorous. Therefore, a few reports have focused on the preparation of soluble aromatic PAEKs. The introduction of a substituent onto the aromatic ring of PAEK is known to be effective to suppress the crystallinity and thus improve the solubility of PAEK. The substituted PAEKs are well soluble in organic solvents, qualified as coating materials and matrix resins with inorganic compounds [4–9].

Usually a cross-linkable group, such as ethynyl [10–13], styryl [14,15], or benzocyclobutene [16], is necessary to be introduced into the amorphous PAEKs for various applications. For example, in fabrication of a waveguide device, crosslinkable PAEKs have several advantages such as increasing thermal stability, chemical resistance, gap filling ability, and improved adhesion properties on the substrates over soluble ones [15,17]. However, for conventional crosslinkable group, the crosslinking reaction does not produce thermoset with satisfying thermal stability due to the remaining of aliphatic residues in the final products. In this paper, a crosslinkable macrocycle of aromatic ether ketone (MCAEK) was synthesized and incorporated into PAEK backbone. The fully aromatic PAEK can undergo cross-linking reaction in the presence of basic initiator via ring-opening.

* Corresponding author. Tel./fax: +86 431 5168886.
E-mail address: jiangzhenhua@mail.jlu.edu.cn (Z. Jiang).

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2. Experimental

2.1. Materials

(3-Methoxy)aniline (Tokyo Chemical Industry), 4,4-difluorobenzophenone (Yanji Chemical Plant), 1,4-benzoquinone (Dalian Jizhou Chemical Reagent), caesium fluoride (Shanghai Zhongli Reagent Co.), 4,4′-(hexafluoroisopropylidene)diphenol (HFBPA) (Shanghai Chemical Reagent), zinc powder (Tianjin Chemical Reagent), hydrochloric acid (36%, Beijing Chemical Reagent), sodium nitrite (Beijing Chemical Reagent), pyridine (Tiantai Chemical Reagent), sodium bicarbonate (Beijing Chemical Reagent), potassium carbonate (Beijing Chemical Reagent), chloroform (Tianjin Chemical Reagent) and toluene (Beijing Chemical Reagent) were used as received. DMAc (Beijing Chemical Reagent) was dried with molecular sieve 4 Å (Guoyao Chemical Reagent).

2.2. Measurements

NMR spectra were recorded on a Bruker 510 instrument with tetramethyl silane as a reference. The FTIR spectra were recorded via the KBr pellet method by using a Nicolet Impact 410 FTIR spectrophotometer. The elemental analysis was carried out with a Thermoquest CHNS-Ovelemental analyzer. The inherent viscosity measurements were carried out with an Ubbelohde viscometer at a concentration of 0.5 g/dL in DMAc at 25 ± 0.1 °C. The gel permeation chromatographic (GPC) analysis was carried out with a Waters 410 instrument with tetrahydrofuran as the eluent and polystyrene as the standard. The glass transition temperatures (T_gs) were determined by using a modulated DSC (Model Mettler DSC821e) instrument at a heating rate of 20 °C/min under a nitrogen flow of 200 mL/min. MALDI-TOF mass spectra were obtained on a Kratos of Shimadzu Company. The thermogravimetric analysis (TGA) was performed on a Perkin–Elmer Pyris 1 analyzer under nitrogen atmosphere (100 mL/min) at a heating rate of 10 °C/min.

2.3. Monomer synthesis

2.3.1. Synthesis of (3-methoxy)phenylbenzoquinone

A 1000 mL beaker equipped with a mechanical stirrer, a dropping funnel, and a thermometer, was filled with water (200 mL), ice and (3-methoxy)aniline (61.5 g, 0.5 mol). Hydrochloric acid (11.8 M, 169.5 mL) was added dropwise into the stirring mixture, and then concentrated water solution (90 mL) of sodium nitrite (34.5 g, 0.5 mol) was added dropwise. The mixture was stirred at 0–3 °C for 2 h and a purple solution was obtained. The resulting solution was filtered and added dropwise to a mixture of 1,4-benzoquinone (54 g, 0.5 mol), sodium bicarbonate (168 g, 2.0 mol) and water (200 mL). The reaction mixture was stirred at 8–12 °C for about 2 h and then at room temperature for 2 h. The precipitate was collected by filtration, washed thoroughly with water, and dried at 60 °C in a vacuum oven for 24 h.

Yield: 90%. Mp: 110 °C (DSC). *m/z*: 214. Elem. Anal. Calcd. for $C_{13}H_{10}O_3$: C, 72.89%; H, 4.71%. Found: C, 71.30%; H, 4.84%. IR (KBr, cm^{-1}): 1657 (C=O), 2830 ($-OCH_3$). ^1H NMR ($CDCl_3$, δ, ppm): 7.39 (t, $J = 9$ Hz), 7.08 (d, $J = 7.5$ Hz, 1H), 7.04 (m, 2H), 6.90–6.85 (m, 3H), 3.87 (s, 3H). ^{13}C NMR ($CDCl_3$, δ, ppm): 187.59, 186.51, 159.49, 145.8, 137.01, 136.17, 133.90, 132.78, 129.59, 121.61, 115.84, 114.71, 55.36.

2.3.2. Synthesis of (3-methoxy)phenylhydroquinone *1*

Obtained (3-methoxy)phenylbenzoquinone (64 g, 0.30 mol), Zn powder (58.9 g, 0.9 mol), and deionized water (550 mL) were placed into a 1000 mL three-necked flask equipped with a mechanical stirrer, a condenser, and a dropping funnel. The mixture was heated to 90 °C with stirring, which was followed by the addition of 72 mL of HCl (11.8 M) dropwise. After addition, the reaction mixture was allowed to reflux for 3 h and the hot mixture was filtered. When the filtrate was cooled to room temperature, pink solid was collected and recrystallized from toluene.

Yield: 71%. Mp: 143 °C (DSC). *m/z*: 216. Elem. Anal. Calcd. for $C_{13}H_{12}O_3$: C, 72.21%; H, 5.59%. Found: C, 71.91%; H, 5.71%. IR (KBr, cm^{-1}): 3403 ($-OH$), 2832 ($-OCH_3$). ^1H NMR (DMSO, δ, ppm): 8.75 (s, 1H), 8.73 (s, 1H), 7.28 (t, $J = 8.5$ Hz, 1H), 7.05 (m, 2H), 6.84 (m, 1H), 6.73 (d, 1H), 6.66 (d, $J = 3.0$, 1H), 6.66 (dd, $J = 9.0$, $J = 3.0$, 1H), 3.77 (s, 3H). ^{13}C NMR (DMSO, δ, ppm): 159.68, 150.90, 147.59, 141.01, 129.73, 128.82, 122.22, 117.72, 117.29, 115.90, 115.61, 112.76, 55.84.

2.3.3. Synthesis of macrocycle with methoxyphenyl *2*

The cyclization was conducted in a 3 L three-necked flask equipped with a Dean–Stark trap, a condenser, a thermometer, and a nitrogen inlet. The reaction vessel was charged with DMAc (1500 mL), toluene (200 mL), and anhydrous potassium carbonate (13.8 g, 0.1 mol). And then, the mixture was stirred and heated to reflux under nitrogen. Then, a DMAc solution (200 mL) of (3-methoxy)phenylhydroquinone 1 (10.80 g, 0.05 mol) and 4,40-difluorobenzophenone (10.90 g, 0.05 mol) was added over 8 h via a syringe pump. After that, the resulting solution was kept under reflux for another 2 h. The reaction mixture was cooled and filtered to remove salts. The filtrate was then concentrated to 100 mL under reduced pressure and added into vigorously stirring distilled water (700 mL) containing 10 mL of concentrated hydrochloric acid. An oligomer was precipitated as a white solid, which was collected by filtration and dried in a vacuum oven at 120 °C for 24 h. The product was separated by column chromatography on silica gel with dichloromethane as eluent.

Yield: 65%. Mp: 246 °C (DSC). *m/z*: 789. Elem. Anal. Calcd. for $C_{52}H_{36}O_8$: C, 79.17%; H, 4.60%. Found: C, 78.90%; H, 4.96%. IR (KBr, cm^{-1}): 1655 (C=O), 1224 (Ar–O–Ar), 2832 ($-OCH_3$). ^1H NMR (DMSO, δ, ppm): 7.73 (d, $J = 9$, 2H), 7.66 (d, $J = 9$, 2H), 7.63 (d, $J = 8.5$, 2H), 7.55 (d, $J = 8.5$, 2H), 7.41 (s, 2H), 7.29 (t, $J = 8$), 7.17–7.10 (m, 8H), 7.08–7.04 (m, 4H), 7.00–6.96 (q, 4H), 6.89 (d, $J = 8.5$, 2H), 3.69 (s, 3H). ^{13}C NMR (DMSO, δ, ppm): 194.12, 162.87, 159.94, 154.27, 150.28, 138.08, 136.19,

133.04, 132.93, 132.44, 130.30, 124.94, 123.97, 122.53, 122.09, 118.85, 118.08, 115.43, 114.26, 55.91.

2.3.4. Synthesis of macrocycle with hydrophenyl **3**

In a 250 mL three-necked flask equipped with a mechanical stirrer, a condenser and nitrogen inlet, macrocycle **2** (3.00 g) and freshly prepared pyridine hydrochloride (100.0 g) were placed. The mixture was heated at 170 °C until the solution became homogeneous after 4 h. After cooling to 120 °C, the mixture was poured into water. The powder was precipitated by pouring the reaction mixture into a blender containing about 250 mL water, then filtered and washed three times with water. A white powder was obtained after drying the precipitate at 80 °C for 24 h in vacuum.

Yield: 96%. *m/z*: 761. Elem. Anal. Calcd. for $C_{50}H_{32}O_8$: C, 78.94%; H, 4.24%. Found: C, 78.61%; H, 4.37%. IR (KBr, cm^{-1}): 1224 (Ar–O–Ar), 1648 (C=O), 3400 (–OH). ^1H NMR (DMSO, δ, ppm): 9.49 (d, $J = 1.0$, 2H), 7.73 (d, $J = 9$, 2H), 7.68 (d, $J = 9$, 2H), 7.64 (d, $J = 8.5$, 2H), 7.59 (d, $J = 8.5$, 2H), 7.36 (d, $J = 3$, 2H), 7.18–7.09 (m, 8H), 7.02–6.94 (m, 10H), 6.72 (d, $J = 8.5$, 2H). ^{13}C NMR (DMSO, δ, ppm): 194.14, 162.91, 158.06, 154.10, 150.41, 138.03, 136.50, 133.03, 132.95, 132.47, 130.21, 124.87, 123.81, 122.36, 120.48, 118.77, 118.23, 116.73, 115.74.

2.4. Synthesis of ring-chain alternated poly(ether ketone)s

The procedure for synthesis of copolymers **4** was as follows. In a 100 mL three-necked round-bottom flask equipped with a mechanical stirrer, a Dean–Stark trap, a condenser, and a nitrogen inlet, macrocycle **3** (1.52 g), 4,4′-difluorobenzophenone (4.36 g), HFBPA (6.05 g), NMP (40 mL), K_2CO_3 (2.80 g), and toluene (20 mL) were placed. Under an atmosphere of nitrogen, the solution was heated to 130 °C and maintained at this temperature for 2 h to remove all water by means of a Dean–Stark trap through toluene. The polycondensation reaction was continued for 5 h at 165 °C. Then the viscous solution was slowly poured into water and stirred vigorously. The threadlike polymer was pulverized into a powder after cooling. Finally, the powder was washed with hot methanol and water several times, and dried at 100 °C under vacuum for 24 h. The copolymer **5** and polymer **6** [18] were prepared through changing the molar ratio of macrocycle **3** and HFBPA to 2:8 and 0:10, respectively, under the same condition as polymer **4**.

2.5. Ring opening polymerization reactions of macrocyclic oligomers

The solid caesium fluoride powder (50 mg) was added into methanol (2 mL). After dissolution, the methanol solution (1 mL) was added into a chloroform solution (6 mL) containing powdered copolymer (**4** or **5**) (0.50 g) and the solution was dispersed further after sonication. The solution was cast onto a clean glass plate and carefully dried at 80 °C for 12 h and then dried in vacuum at 120 °C for 24 h. The resulting films were heated for 1 h at 270 °C under nitrogen. The cured polymer was extracted with chloroform for 3 days and methanol for 3 days, and then dried for 2 days at 120 °C under vacuum.

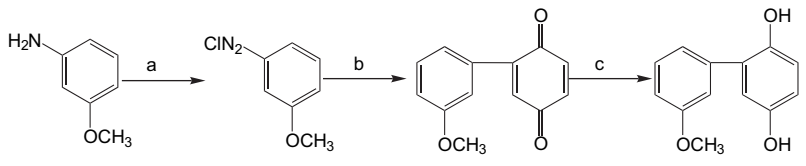
3. Results and discussion

3.1. Synthesis of (3-methoxy)phenylhydroquinone **1**

As shown in Scheme 1, the bisphenol was synthesized in a three-step synthetic process including the diazonium reaction of *m*-anisidine in the presence of hydrochloric acid and sodium nitrite, the coupling reaction of 3-methoxy-phenyldiazonium chloride with benzoquinone to yield (3-methoxyphenyl)benzoquinone and the reduction of (3-methoxyphenyl) benzoquinone with Zn/HCl in boiling water. The bisphenol was obtained as purple crystal after the recrystallization in toluene and its structure was identified by mass spectrometry, IR and NMR spectroscopies. In the IR spectrum, (3-methoxy)phenylbenzoquinone showed an absorption band at around 1657 cm^{-1} attributed to the symmetric stretching vibration of carbonyl groups. After reduction, this characteristic absorption disappeared, and the characteristic band of hydroxyl group at around 3308 cm^{-1} was identified. In the ^1H NMR, the signals at 8.75 ppm and 8.73 ppm were assigned to the hydroxyl proton, which could not be observed in the spectrum of the corresponding quinone. The peaks at 2.40 ppm and 7.28–6.66 ppm are assigned to the methoxy and aromatic protons, respectively. ^{13}C NMR spectra of (3-methoxy)phenylbenzoquinone and (3-methoxy)phenylhydroquinone all exhibit 13 peaks, and the peak at ~55 ppm is assigned to methoxy carbon atoms.

3.2. Synthesis of macrocycle monomer

Under pseudo-high dilution condition, the macrocyclic aromatic ether ketone oligomers were prepared by aromatic nucleophilic substitution from bisphenol **1** and 4,4′-difluorobenzophenone (Scheme 2). The pseudo-high dilution condition



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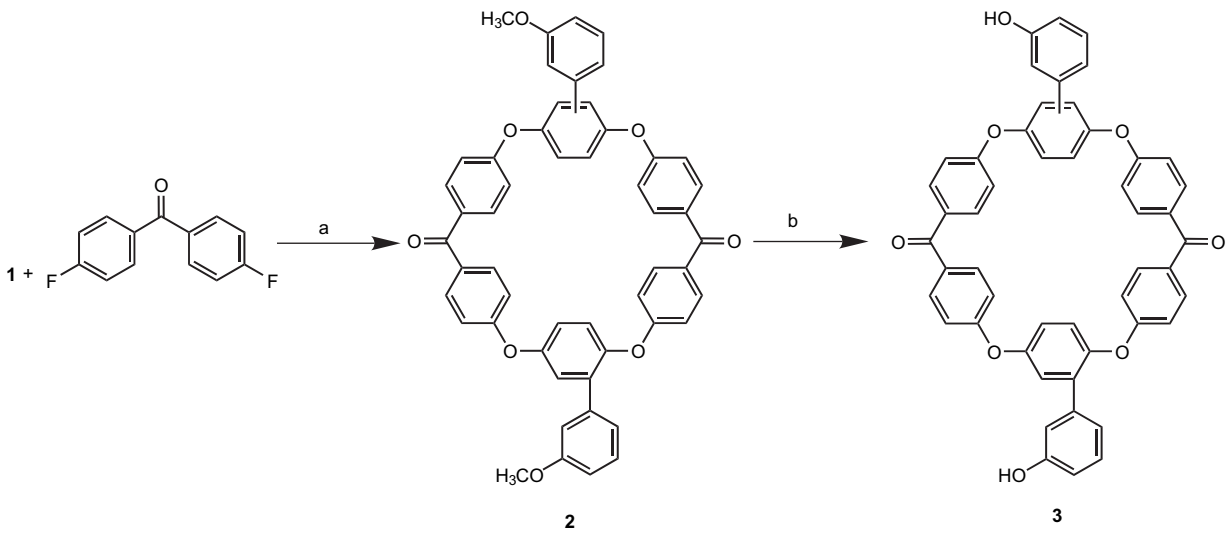
Scheme 1. Synthetic procedure for the (3-methoxy)phenylhydroquinone **1**. (a) HCl, $NaNO_2$; (b) benzoquinone, $NaHCO_3$; (c) Zn, HCl.



Scheme 2. Synthetic procedure for the macrocycles **2** and **3**. (a) K_2CO_3, DMAc, toluene; (b) pyridine hydrochloride.

was achieved by slowly dropping the solution of the reactants mentioned above to a large amount of solvent containing K_2CO_3 through syringe. The main product, macrocycle **2**, was isolated chromatographically as pure compound. Direct confirmation of the macrocycle **2** was provided by employing the matrix-assisted laser desorption/ionization-time of flight-mass spectrometry (MALDI-TOF-MS). The only one signal of pure product at 789.4 corresponds to the molecular weight of macrocycle **2** (Fig. 1a). The IR spectrum of the macrocycle **2** showed the characteristic absorption bands at around 1660 cm^{-1}, 1220 cm^{-1} and 2832 cm^{-1} assigned to symmetric stretching vibration of aryl carbonyl groups, asymmetric stretching vibration of aryl ether linkages and symmetric stretching vibration of methoxy moieties, respectively.

In the ^1H NMR spectrum, the chemical shifts and assignments were in consistent with the expected structure of the macrocycle (Fig. 2). In the spectrum, four groups of symmetry double peaks in the range from 7.73 ppm to 7.55 ppm were assigned to hydrogen *ortho* to carbonyl in macrocycles. The appearance of the four groups of double peaks is likely to be attributed to the changed shielding effect of the nucleus by the steric effect in the macrocycle. In the ^{13}C NMR spectrum, the C4 also presents two different chemical shifts attributed to the steric impact of the macrocycle (Fig. 2) [19].

The macrocycle **3** was obtained with high purity and high yield by demethylation of macrocycle **2** in molten pyridine hydrochloride. The structure of macrocycle **3** was identified by MALDI-TOF-MS (Fig. 1b), IR and ^1H NMR spectroscopies. In the IR spectrum, the characteristic absorption of methoxy group at around 2832 cm^{-1} disappeared and the characteristic band of hydroxyl group at around 3270 cm^{-1} appeared. In the NMR spectrum, the signal at 9.49 ppm was assigned to the hydroxyl proton which was absent in the spectrum of macrocycle **2**, the signals at 7.73–7.59 were assigned to the hydrogen *ortho* to carbonyl in macrocycles, which also consist of four groups of double peaks similar to macrocycle **2** (Fig. 3a). In the ^{13}C NMR spectrum, there were 19 signals from the 17 types of carbons due to the steric impact (Fig. 4).

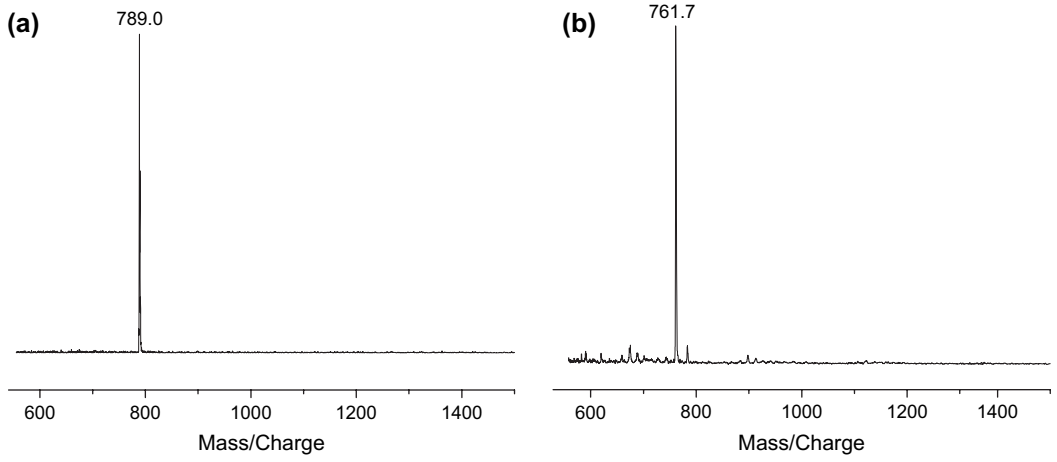


Fig. 1. Positive ion MALDI-TOF-MS spectra: (a) macrocycle **2**, M = 788; (b) macrocycle **3**, M = 760. The matrix used for the experiments was 1,8,9-anthracenetriol (dithranol).

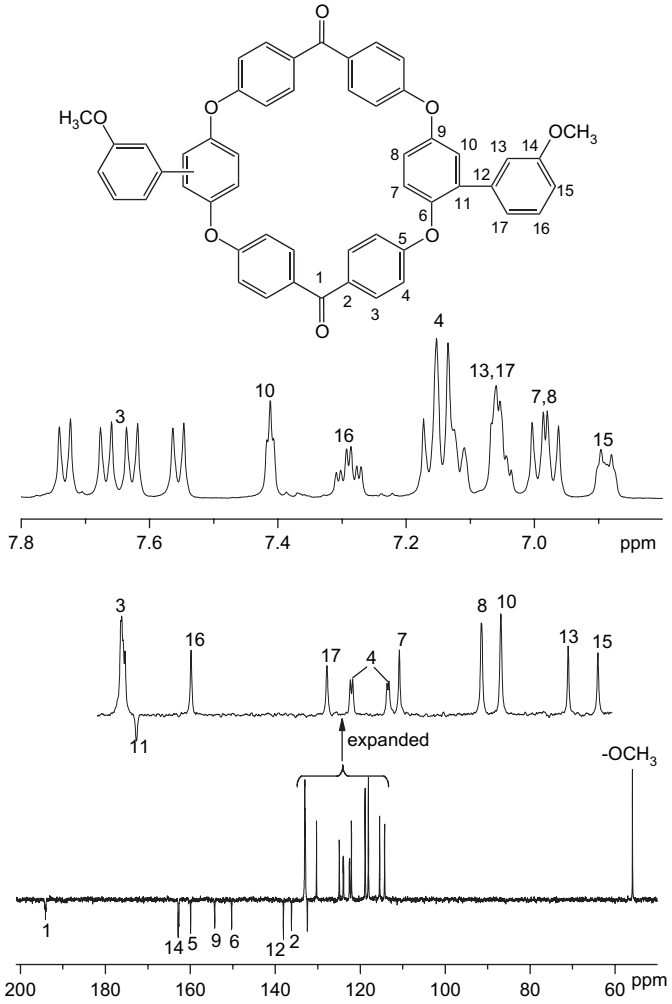


Fig. 2. ^{1}H NMR and ^{13}C NMR spectra of macrocycle **2** (DMSO-d_6).

3.3. Synthesis of copolymers

The PAEKs containing MACEK were prepared from macrocycle **3**, HFBPA, and 4,4-difluorobenzophenone in the presence of potassium carbonate by nucleophilic polycondensation as shown in Scheme 3. After redissolving in chloroform and then coagulation in ethanol, the copolymers were purified. Viscosity and GPC characterization, listed in Table 1, demonstrated that obtained copolymers had high molar mass, which indicated that the macrocyclic hindrance had little influence on the reaction activity of **3** during polycondensation. The glass transition temperature (T_g) and the thermal stability of the copolymers have been investigated with differential scanning calorimetry (DSC) (Fig. 5) and thermogravimetric analysis (TGA) measurements under nitrogen. Copolymers **4** and **5** both are amorphous polymers. The glass transition temperature (T_g) of copolymer **5** (177 °C) was higher than that of copolymer **4** (160 °C). The high T_g of this copolymer is interpreted in terms of the increased macrocycle ratio. The introduction of macrocycle as a rigid group will result in difficulties in fragment movement, which caused higher T_g. The 5 wt% weight loss temperatures of these copolymers are above 500 °C, indicating their good thermal stability (Table 1).

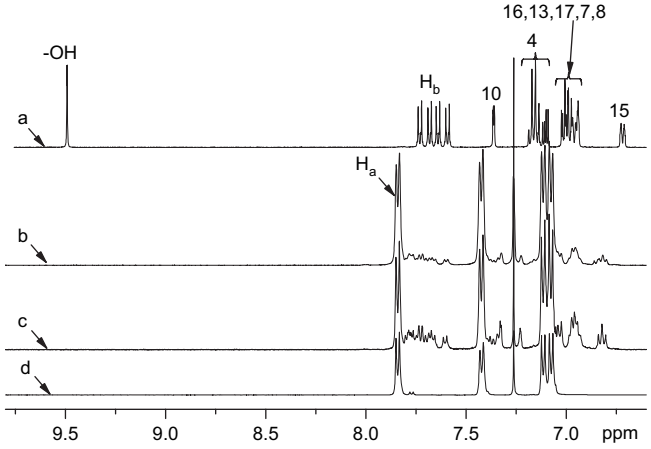


Fig. 3. ^{1}H NMR spectra of 500 M: (a) macrocycle **3** (DMSO-d_6); (b) copolymer **4** ($CDCl_3$); (c) copolymer **5** ($CDCl_3$); (d) polymer **6** ($CDCl_3$).

^{1}H NMR analysis was employed to further investigate the structure of the cyclic product. The ring strain changes the electron cloud distribution of the macrocycle, and in consequence changes the chemical shifts of the protons in *ortho*-position of carbonyl in macrocycles (H_b) (Scheme 3) to higher field [19]. Fig. 3b and c shows the ^{1}H NMR spectra of the copolymers **4** and **5**. The peaks corresponding to the protons in *ortho*-position of carbonyl in macrocycles (H_b) or in chains (H_a) were well separated from each other, which confirmed the existence of macrocycle structure in the copolymers. However, there was only one single peak from the protons in *ortho* to carbonyl in the ^{1}H NMR spectrum of polymer **6** (Fig. 3d).

3.4. Cross-linking reaction of copolymer via ring-opening

The MCAEK can be transformed into high molar linear polymer via ring-opening polymerization [19–23]. It is known

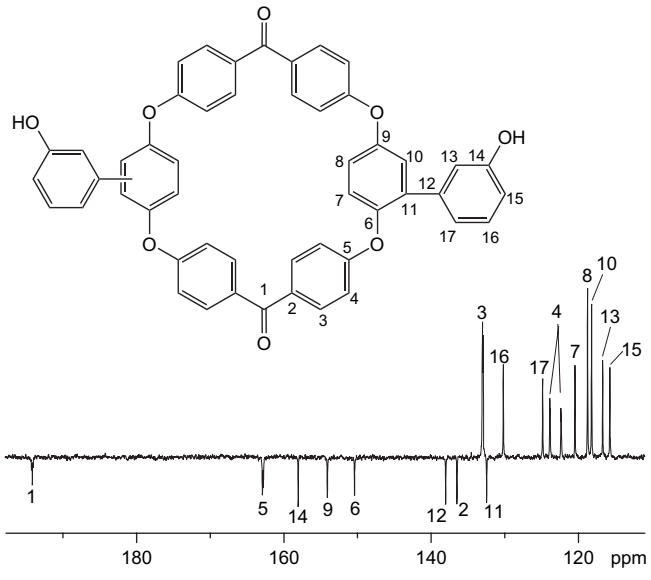
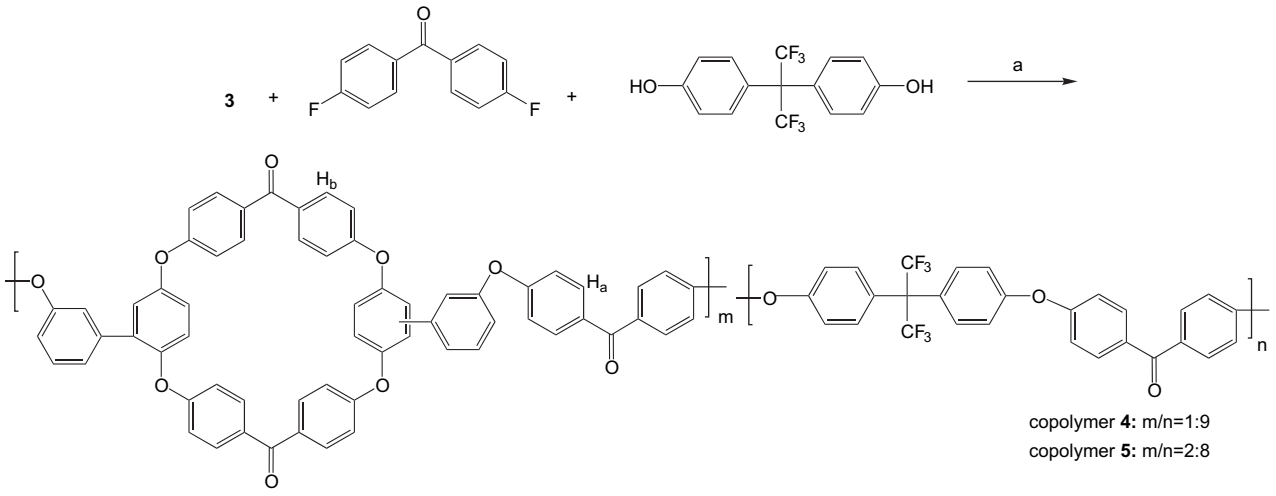


Fig. 4. ^{13}C NMR spectra of macrocycle **3** (DMSO-d_6).



Scheme 3. Synthetic route of the copolymers **4** and **5**. (a) K_2CO_3, NMP, toluene.

that the ring-opening reaction of the macrocycle is initiated by nucleophilic attack of the fluoride ion or phenoxy anion on the carbon of aromatic nuclei [24,25] and proceeds as a transetherification reaction driven by the entropic change due to its neglectable ring strain [26]. The crosslinking reaction of the copolymers was similar to the ring-opening reaction of MCAEK. As illustrated in Scheme 4, in the reaction, (i) a fluorine anion attacks the ketone-activated ether linkages of a macrocycle, opening the ring and (ii) generating a new phenoxide end group, which attacks ketone-activated ether linkages of another macrocycle, (iii) the combination of double macrocycle results in crosslinking reaction. Ring-opening polymerizations were carried out at 270 °C for 1 h. DSC scans showed that the glass transition temperatures (T_gs) of the cured samples increased greatly compared to the original film samples (Fig. 5). T_g of copolymer **4** increased from 160 °C to 180 °C and that of copolymer **5** increased from 177 °C to 204 °C after the curing.

The cured copolymers became completely insoluble in common organic solvents such as DMAc, THF, and only swelled slightly in concentrated sulfuric acid. To examine the gel fraction of the cured polymer, the film cured at 270 °C for 1 h was extracted with chloroform and methanol and then dried under vacuum. It was found that cured copolymer **4** has a gel fraction of 71%, cured copolymer **5** has a gel fraction of 86%. When the linear poly(ether ketone) without macrocycle structure (polymer **6**) from HFBPA and 4,4-difluorobenzophenone was treated under the same curing condition, there was no any change of its T_g and solubility (Fig. 5). This suggests that the crosslinking reaction of the copolymer **4** or **5** goes via the ring opening reaction of the macrocycles during the heating treatment. Such ring-opening reaction is likely to be driven by entropy change since the copolymers are allowed to adopt more conformations after the opening of the macrocycle [26]. No crosslinking reaction of polymer **6** could be identified under the same curing condition. This is reasonable since no increase in entropy could be expected for polymer **6** before and after the curing. The cured copolymers **4** and **5** had excellent stability against thermal decomposition. Their temperatures at a 5% weight loss were 500 °C for copolymer **4**, 502 °C for copolymer **5** in nitrogen. The highly thermal stability is attributed to the fully aromatic structure of the copolymer.

Table 1
Properties of the copolymers **4**, **5** and polymer **6**

Polymer	η_{inv} [a] (dL/g)	M_n [b]	Polydispersity	T_g (°C)	TGA-5% (°C)
4	0.60	43 000	2.7	160	521
5	0.52	30 000	3.2	177	529
6	0.79	55 000	2.0	168	524

[a] Measured at a concentration of 0.5 g/dL in DMAc at 25 ± 0.1 °C.
[b] Molecular weights of the copolymers were calculated with the aid of polystyrene standards.

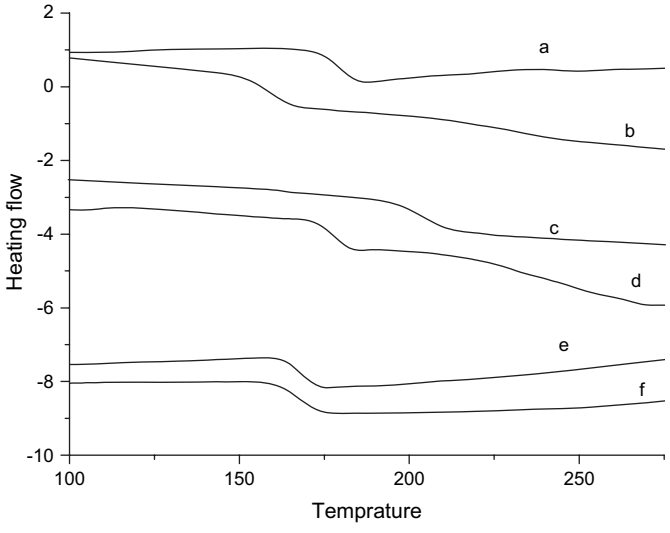
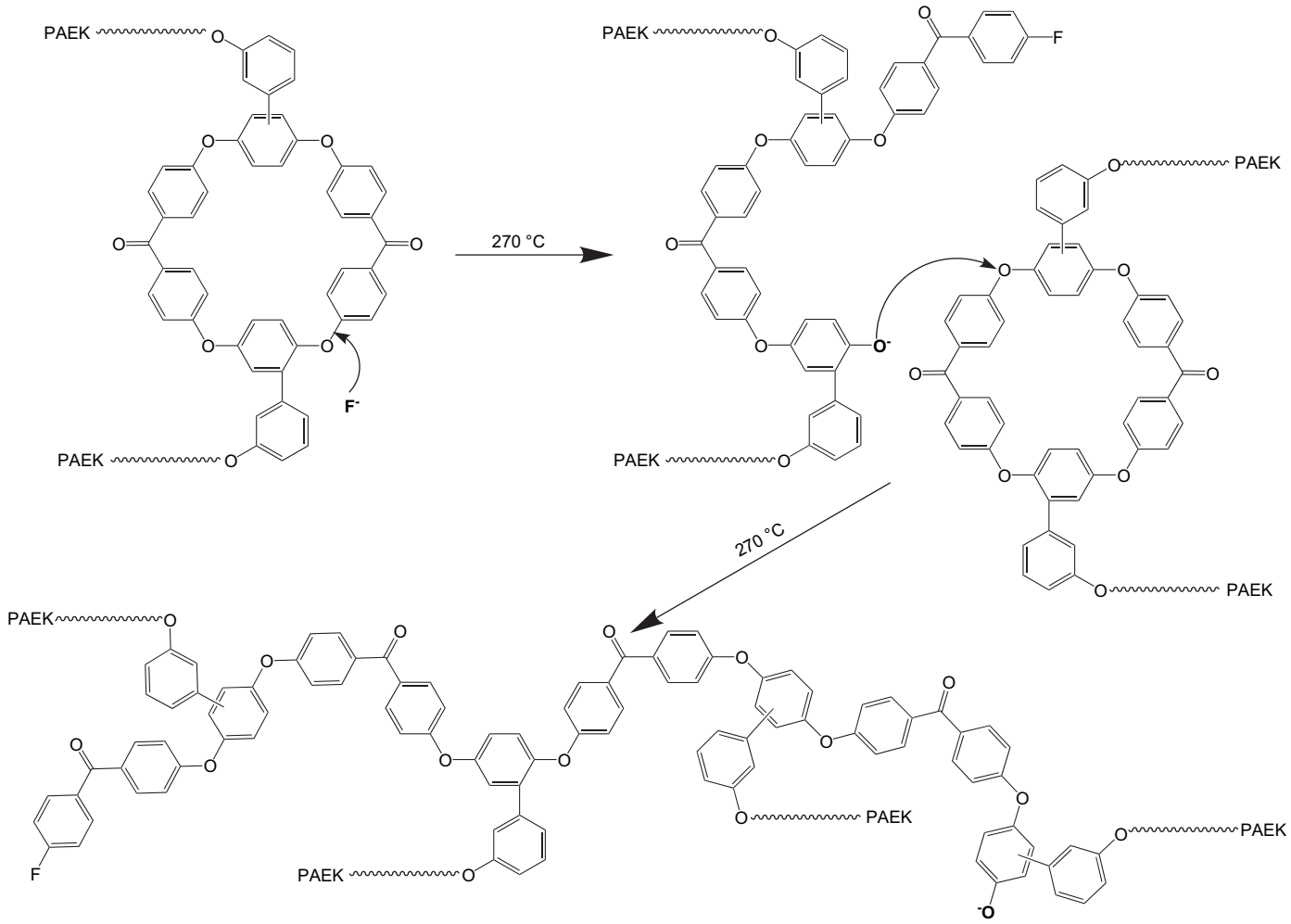


Fig. 5. DSC curves of the polymers: (a) cured copolymer **4**; (b) copolymer **4**; (c) cured copolymer **5**; (d) copolymer **5**; (e) polymer without the macrocycle after heating treatment; (f) polymer without the macrocycle.



Scheme 4. Schematic representation of the crosslinking reaction. The crosslinking reaction of the copolymers was carried out under 270 °C in the presence of CsF.

4. Conclusion

A novel bisphenol, (3-methoxy))phenylhydroquinone was prepared via a three-step reaction. Based on this monomer, a cross-linkable macrocycle of aromatic ether ketone (MCAEK) was synthesized and incorporated into PAEK backbone. The copolymers can go cross-linking reaction in the presence of basic initiator. The glass transition temperatures of the copolymers increased greatly after the curing. The cured copolymers became completely insoluble in common organic solvent and exhibited outstanding thermal stability. Such work provides a new approach to prepare crosslinkble poly(arylene ether ether)s with fully aromatic structure.

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