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Communications to the Editor

Large-Sized Macrocyclic Monomeric Precursors of Poly(ether ether ketone): Synthesis and Polymerization

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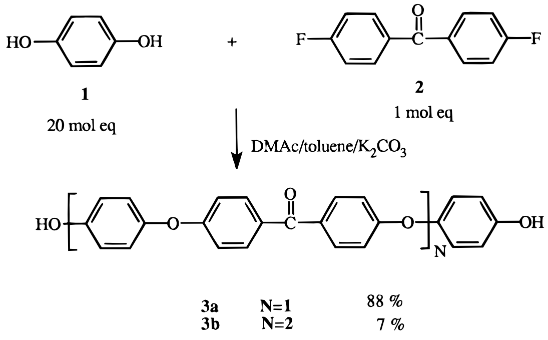
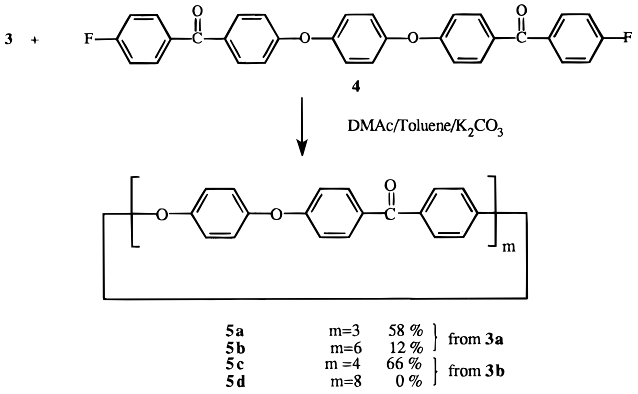
Scheme 1



Scheme 2



Introduction. The recent discovery by Brunelle and co-workers[1] of the high-yield synthesis and facile polymerization of Bisphenol-A-based cyclic polycarbonate has sparked much interest in the macrocyclic monomer technique. The advantages of using macrocyclic precursors have been recognized in several aspects, i.e., low melt viscosity, rapid melt ring-opening polymerization without generating volatile side products. These features are particularly valuable for the manufacture of advanced composite materials. In the last several years, this area has been rapidly extended to other systems such as cyclic esters,[2] amides,[2,3] ether imides,[2] ether ketones,[4−6] ether sulfones,[7−9] and thioether ketone.[10] However, only a few pure single-sized macrocycles were isolated and characterized. In addition, the polymers obtained by ring-opening polymerization of the macrocyclic monomers were generally amorphous.

Poly(ether ether ketone) (PEEK) is a very important, commercially available, high-performance, semicrystalline thermoplastic widely known for its excellent mechanical properties and thermal and environmental stability.[11] The commercial process of preparing PEEK is through the aromatic nucleophilic substitution reaction of 4,4′-difluorobenzophenone with hydroquinone at a polymerization temperature near its melting point.[12,13] We were interested in producing PEEK through ring-opening polymerization of macrocyclic precursors.[14] Herein, we disclose our preliminary results in this endeavor.

Results and Discussion. A two-step method was adopted as with our previously reported work.[15−16] First, aromatic bisphenols, **3**, were synthesized by reaction of 4, 4′-difluorobenzophenone (**2**) with a large excess of hydroquinone (Scheme 1). **3a** and **3b** can be easily separated by their solubility difference in acetone; **3a** is soluble in acetone, but **3b** is not. The structures of **3a**[17] and **3b**[18] were confirmed by NMR and MS. The second step is cyclization of the bisphenol with difluoro ketone compound **4**, which was synthesized from Friedel−Crafts acylation of 4,4′-diphenoxybenzene with 4-fluorobenzoyl chloride.[19] The cyclization reaction (Scheme 2) was carried out in *N*,*N*-dimethylacetamide (DMAc) under pseudo-high-dilution conditions. K_2CO_3 was used as base. The refluxing temperature was controlled at 135 °C by varying the amount of the azeotropic solvent toluene. The syringe pump technique was not used because **4** is not soluble in DMAc at room temperature. Equivalent amounts[20] of **3** and **4** were added in four batches over a period of 36 h to the refluxing solvent reservoir containing K_2CO_3. The total reaction time was about 65 h. Pure cyclic products free from linear oligomers were isolated by exhaustive extraction of the crude product with chloroform, since the linear PEEK oligomers are totally insoluble in chloroform. When **3a** was used, the product was a mixture of "single-sized" (1 + 1), 45-membered **5a** and "double-sized" (2 + 2), 90-membered **5b** (total cyclic yield 70%; **5a**,[21] 58%; **5b**,[22] 12%), which were separated by column chromatography with a silica gel column and methylene chloride as eluent. When **3b** was used, a "single-sized", 60-membered macrocycle (**5c**[23]) was obtained in a yield of 66%. The "double-sized", 120-membered macrocycle **5d** was not observed due to precipitation of longer linear oligomers.

The structures of the macrocycles were confirmed by ^1H and ^{13}C NMR and FABMS techniques. Figure 1 shows the ^1H NMR spectra of the ether ether ketone macrocycles with different sizes. All of them show the same pattern (two doublets and one singlet), although the chemical shifts are significantly different. No terminal group was detected in the spectra, indicating the cyclic structure of each compound. The FABMS spectra completely match the calculated molecular weights for each of these macrocycles.[21−23] Figure 2 gives the FABMS of macrocycle **5c**, which shows the pseudo molecular ion ($[M + H]^+$) peak at $m/z = 1153.6$ (calculated 1153.3).

The macrocycles have thermal stabilities comparable to that of PEEK. For example, **5c** has a 5% weight loss temperature of 596 °C in nitrogen and 561 °C in air.

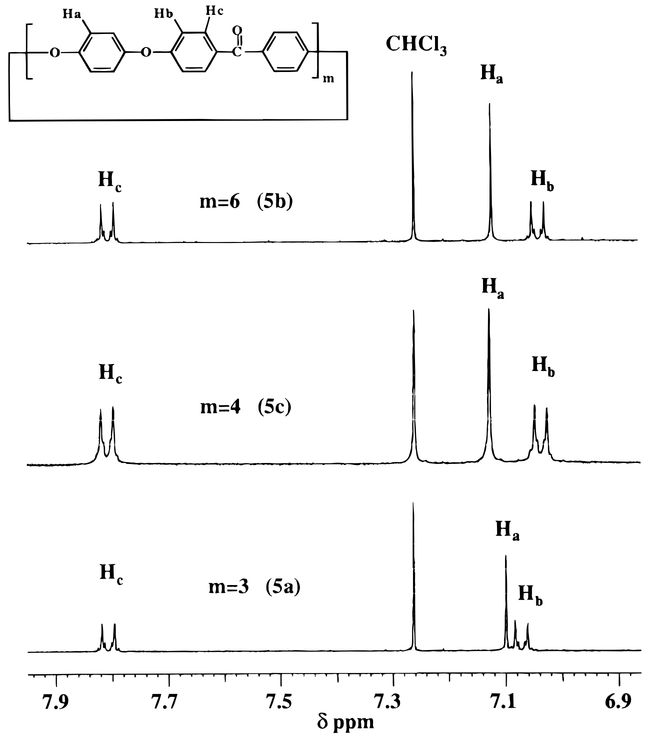


Figure 1. 400 MHz ^{1}H NMR spectra of **5a**−**c** in CDCl$_3$.

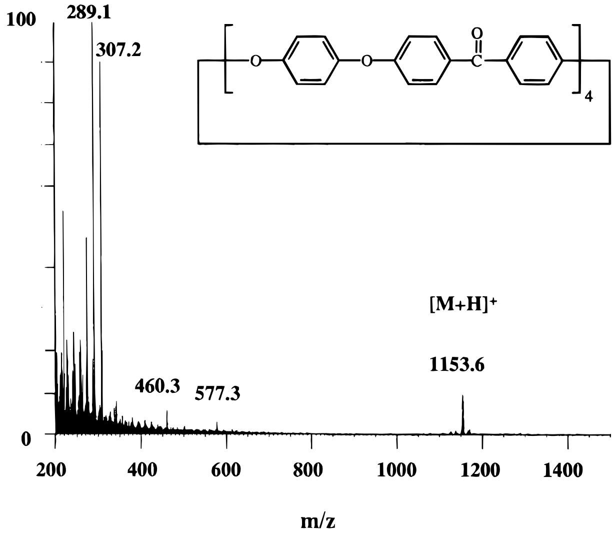


Figure 2. FABMS spectrum of **5c** in 3-NBA matrix.

The polymerizations of the macrocycles were carried out in vacuum at temperatures above the melting points with different initiators. When CsF was used, the polymer obtained was insoluble in concentrated H_2SO_4, indicating that the polymer was slightly cross-linked. Figure 3 compares the DSC thermograms of a mixture of **5a** and **5b** and the sample bulk polymerized at 350 °C with 2% (weight) CsF for 5 min. The polymer showed a melting point peak at 335 °C and a glass transition temperature (midpoint) of 152 °C. These transition temperatures are typical of commercial semicrystalline PEEK. We were not able to get a soluble polymer when CsF was used under various conditions. However, when sodium 4-phenoxyphenoxide was used, soluble polymer was obtained. For example, **5c** was polymerized with 2.0% (weight) sodium 4-phenoxyphenoxide at 340 °C for 10 min to give a polymer with an intrinsic viscosity of 0.55 dL/g (measured in 96% sulfuric acid at 30 °C).

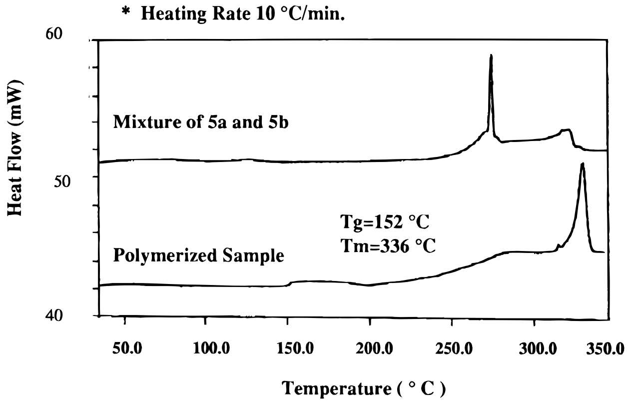


Figure 3. DSC thermogram of a mixture of **5a** and **5b** compared to that of a polymerized sample.

Conclusions. We have reported a concise synthesis of 45-, 60-, and 90-membered macrocyclic monomers for commercially important PEEK polymer. Elsewhere we reported the synthesis and characterization of the 30-membered homolog.[24] This approach has the features of high yield, easy separation of the cyclics from the linear oligomers, and no contamination from linear oligomers. The structures of the macrocycles were confirmed by NMR and FABMS spectra. We also have demonstrated that high-performance semicrystalline PEEK polymer can be produced by ring-opening polymerization of macrocyclic monomers. Further work will be directed toward optimization of the cyclization reaction, detailed polymerization study, and mechanical testing of the bulk-polymerized samples.

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(17) **3a**: mp 227 °C (by DSC); ^{1}H NMR (acetone-d_6): δ 7.78 (d, J = 8.8 Hz, 4H), 7.01 (d, J = 8.8 Hz, 4H), 7.00 (d, J = 8.8 Hz, 4H), 6.91 (d, J = 8.8 Hz, 4H); CIMS [M + H]$^+$, determined 399.0, calculated 399.1.

(18) **3b**: mp 255 °C (by DSC); ^{1}H NMR (DMSO-d_6) δ 9.52 (s, 2H, OH), 7.77 (d, J = 8.8 Hz, 4H), 7.74 (d, J = 8.8 Hz, 4H), 7.25 (s, 4H), 7.12 (d, J = 8.8 Hz, 4H), 6.99 (d, J = 8.8 Hz, 8H), 6.83 (d, J = 8.8 Hz, 4H); FABMS [M + H]$^+$, determined 687.0, calculated 687.2.

(19) Kricheldorf, H. R.; Delius, U. *Macromolecules* **1989**, *22*, 517. No ferric chloride was used. Our yield (95%) and melting point (232.1−235.3 °C) were significantly higher than reported.

(20) Total monomer concentration at end of addition if no reaction had occurred: **3a**, 6.6 mM; **3b**, 1.9 mM.

(21) **5a**: mp 366 °C (by DSC at 10 °C/min); ^{1}H NMR (CDCl$_3$) δ 7.81 (d, J = 8.8 Hz, 12H), 7.10 (s, 12H), 7.07 (d, J = 8.8 Hz, 12H); FABMS [M + H]$^+$, determined 864.2, calculated 864.2.

(22) **5b**: mp 324 °C (by DSC at 10 °C/min); ^{1}H NMR (CDCl$_3$) δ 7.81 (d, J = 8.8 Hz, 24H), 7.13 (s, 24H), 7.05 (d, J = 8.8Hz, 24H); FABMS [M + H]$^+$, determined 1729.6, calculated 1729.5.

(23) **5c**: mp 333 °C (by DSC at 10 °C/min); ^{1}H NMR (CDCl$_3$) δ 7.81 (d, J = 8.8 Hz, 16H), 7.13 (s, 16H), 7.04 (d, J = 8.8 Hz, 16H); FABMS [M + H]$^+$, determined 1153.6, calculated 1153.3. This melting point corresponds to that observed at 5 °C/min by Jonas and Legras[14] for what they believed was the cyclic tetramer, i.e., **5c**.

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