Macrocyclic Ring−Chain Poly(ether ketone)s

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Introduction

The discovery of macrocyclic aromatic ether ketones and ether sulfones has enabled ring-opening polymerization to be investigated as an approach to the synthesis and in situ fabrication of high-performance aromatic polymers.[1] However, beyond the ether-interchange reaction leading to polymerization,[2] little is known of the chemistry of these macrocycles.[3,4] We now report the synthesis of all-aromatic ring−chain poly(ether ketone)s by electrophilic polyaroylation of the cyclic dimer formed by cyclo-condensation of resorcinol with 4,4′-difluorobenzophenone.

Results and Discussion

The products of Scheme 1, from [2 + 2] cyclic dimer to [16 + 16] cyclic hexadecamer, were identified by MALDI-TOF mass spectrometry. Macrocycles **1**−**4** were isolated chromatographically as pure compounds, although the cyclodimer **1** (mp 381 °C, 12% yield) could also be crystallized directly from the reaction mixture. Single-crystal X-ray analyses[5] of **1** and **3** confirmed the cyclic nature of these oligomers (Figure 1).

The presence of two potentially reactive resorcinol residues in **1** suggested that this molecule might undergo linear polycondensation with bis-electrophiles such as diaroyl chlorides. To test this idea, a model reaction was carried out in which macrocyle **1** was treated with 4-chlorobenzoyl chloride in the presence of aluminum chloride (Scheme 2). Diaroylation of the macrocycle occurred in high yield, affording equal quantities of *syn*- and *anti*-isomers **5a** and **5b**, respectively, which were separable by chromatography. The slower-running compound was identified by single-crystal X-ray analysis[6] as the *anti*-isomer **5b** (Figure 2).

This model reaction confirmed that macrocycle **1** can behave as a difunctional reactant in electrophilic aromatic substitution, and so polymerization reactions involving **1** and the diaroyl chlorides 4,4′-biphenyldicarbonyl chloride, 4,4′-hexafluoroisopropylidenedibenzoyl chloride, and 4,4′-oxydibenzoyl chloride were next attempted (Scheme 3). In all three cases polymer precipitated in gel-like form during the reaction and left a tough, transparent film on the walls of the flask. These films gave well-resolved IR spectra showing no evidence of aliphatic C−H groups, confirming the absence of possible side reactions involving dichloroethane.[7]

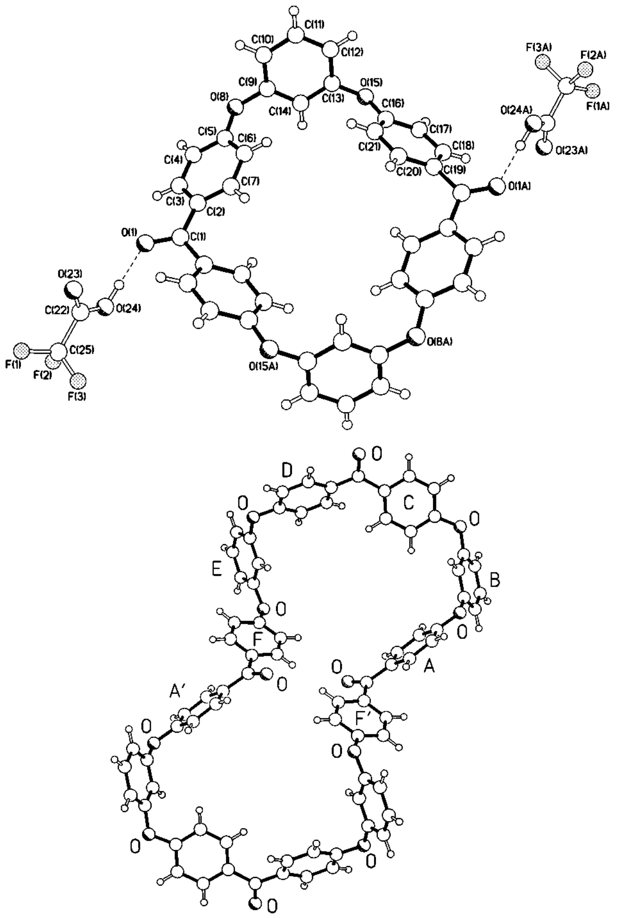
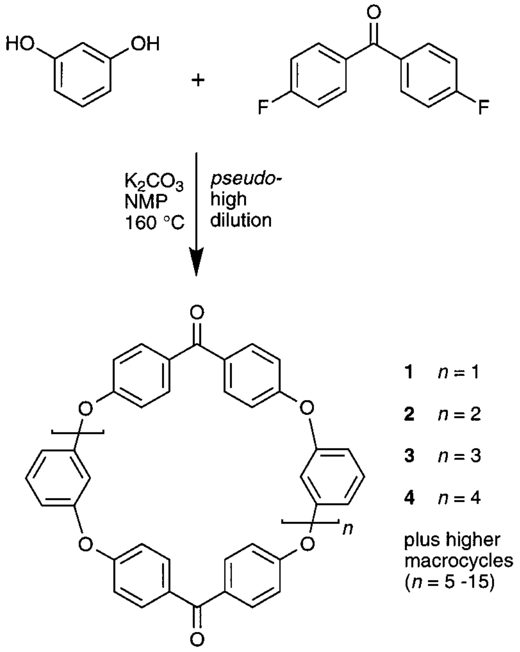


Figure 1. X-ray structures (a) of the [2 + 2] cyclic dimer **1** (top) showing the hydrogen-bonded trifluoroacetic acid and (b) of one of the two independent molecules of the centrosymmetric [4 + 4] cyclic tetramer **3** (bottom).

Scheme 1



Polymers **6**−**8** are soluble in aprotic solvents such as dimethylacetamide (DMAc) and chloroform. Viscometric

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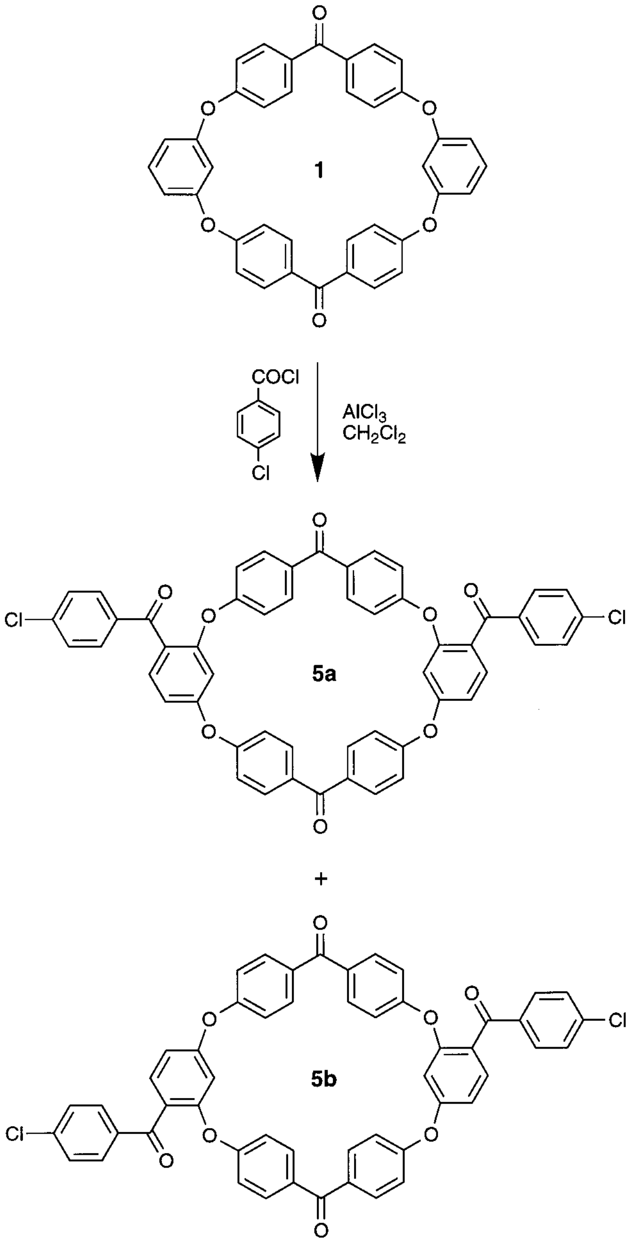
Scheme 2



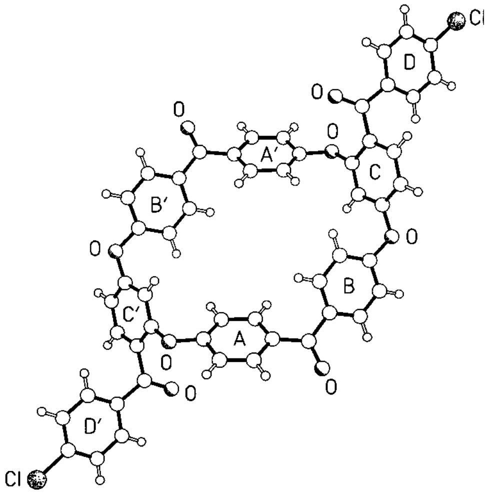
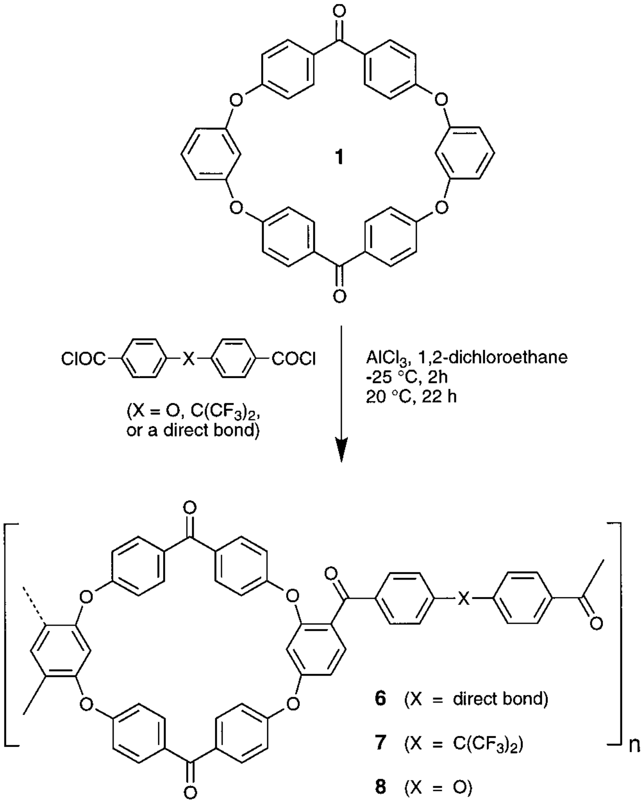


Figure 2. X-ray structure of the centrosymmetric *anti*-bis-(4-chlorobenzoyl) macrocycle **5b**.

Scheme 3



and GPC data demonstrated that high molar mass polymers had been obtained, and DSC indicated that the polymers were amorphous, with high glass transition temperatures (T_g = 283 °C for **6**, 257 °C for **7**, and 244 °C for **8**). ^{1}H and ^{13}C NMR data confirmed that the macrocyclic ring structure had been retained in these polymers and were consistent with chains containing random sequences of *syn*- and *anti*-substituted macrocycles.

Experimental Section

Cyclo-polycondensation of Resorcinol with 4,4′-Difluorobenzophenone. A solution of resorcinol (5.50 g, 0.05 mol) and 4,4′-difluorobenzophenone (10.90 g, 0.05 mol) in 70 cm^3 of *N*-methylpyrrolidone (NMP) was added via syringe pump (4 cm^3/h) under nitrogen to a stirred, refluxing mixture of toluene (40 cm^3), NMP (90 cm^3), and potassium carbonate (15.0 g, 0.13 mol). Water was continuously removed during the addition via a Dean-Stark apparatus, and reaction was continued at 160 °C for a further 12 h. The solution was filtered while hot, and after standing for 48 h crystals of the [2 + 2] cyclic dimer **1** were filtered off and recrystallized from NMP (1.65 g, 11.5% yield, mp 381 °C). The filtrate was added to 10% hydrochloric acid, and the resulting precipitate was filtered off, washed with water and methanol, and dried (12.0 g). This material, (3.50 g) was chromatographed on silica gel with 2% (v/v) ethyl acetate in dichloromethane to give [3 + 3] cyclic trimer **2** (0.22 g, 5.2% yield, mp 267 °C), [4 + 4] cyclic tetramer **3** (0.14 g, 3.3% yield, mp 278 °C), and [5 + 5] cyclic pentamer **4** (0.03 g, 0.7% yield, amorphous).

Bis-chlorobenzoylation of Macrocycle 1. A dichloromethane solution (25 cm^3) containing macrocycle **1** (1.38 g, 0.0024 mol) and 4-chlorobenzoyl chloride (1.45 g, 0.0083 mol) under nitrogen was cooled to −20 °C. Aluminum chloride (4.25 g, 0.032 mol) was added with stirring, and the temperature was raised to 20 °C over 2 h. After a further 6 h the solution was added to water (200 cm^3), and the resulting suspension was heated to drive off the dichloromethane. Macrocycle **5** (1.98 g, 97% yield) was recovered by filtration and characterized by FAB-MS and by ^{1}H NMR. The *syn*- and *anti*-isomers **5a** and

5b were separated by column chromatography on silica gel with dichloromethane as eluent, and the slower-runing *anti*-isomer **5b** was characterized by ^1H and ^{13}C NMR, FAB mass spectrometry, and single-crystal X-ray analysis. Crystals of **5b** were grown by vapor diffusion of hexane into a solution in 1,2-dichlorobenzene/trifluoroacetic acid.

Polycondensation of Macrocycle 1 with 4,4′-Hexafluoroisopropylidenedibenzoyl Chloride. A solution containing the cyclic dimer **1** (0.460 g, 0.8 mmol), aluminum chloride (1.20 g, 9.0 mmol), 4,4′-hexafluoroisopropylidenedibenzoyl chloride (0.342 g, 0.8 mmol), and DMF (0.142 g, 1.95 mmol) in 1,2-dichloroethane (16 cm^3) was stirred at −25 °C for 20 min and then warmed to 25 °C over 2 h. After stirring for a further 20 h a gel-like product had precipitated, and a transparent film of polymer had formed on the walls of the flask. The gel was separated, solidified by treatment with methanol, milled to a powder, extracted with methanol at reflux, and dried. The resulting polymer **7** (0.70 g, 94% yield) had inherent viscosity (η_{inh}) 1.41 dL g^{-1} (0.2% w/v at 25 °C in concentrated sulfuric acid) and was soluble in chloroform, THF, and dimethylacetamide. Analysis by GPC (polystyrene standards) gave $M_w = 67\,000$ and $M_n = 30\,000$. Reactions with 4,4′-biphenyldicarbonyl chloride and 4,4′-oxydibenzoyl chloride were carried out under similar conditions and gave polymers **6** and **8**, with $\eta_{inh} = 1.08$ and 1.04 dL g^{-1}, respectively.

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Supporting Information Available: MALDI-TOF mass spectrum of the family of macrocycles formed by reaction of resorcinol with 4,4′-difluorobenzophenone; ^1H and ^{13}C NMR data for macrocycles **1** and **5b** and for polymer **7**; full crystallographic data for **1**, **3**, and **5b**. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) (a) Brunelle, D. J. In *New Methods of Polymer Synthesis*; Ebdon, J. R., Eastmond, G. C., Eds.; Blackie: London, 1995; p 197. (b)Wang, Y. F.; Chan, K. P.; Hay, A. S. *React. Funct. Polym.* **1996** *30*, 205. (c) Hodge, P.; Colquhoun, H. M.; Williams, D. J. *Chem. Ind. (London)* **1998**, 162.

(2) (a) Colquhoun, H. M.; Dudman, C. C.; Thomas, M.; O'Mahoney, C. A.; Williams, D. J. *J. Chem. Soc., Chem. Commun.* **1990**, 336. (b) Chen, M.; Gibson, H. W. *Macromolecules* **1996**, *29*, 5502. (c) Yokoi, Y.; Yamamoto, K.; Tsuchida, E.; Hay, A. S. *Macromolecules* **1997**, *30*, 4502. (d) Jiang, H. Y.; Chen, T. L.; Qi, Y. H.; Xu, J. P. *Polym. J.* **1998**, *30*, 300. (e) Teasley, M. F.; Wu, D. Q.; Harlow, R. L. *Macromolecules* **1998**, *31*, 2064.

(3) Friedel−Crafts chemistry has however been developed for other types of macrocycles—for example, the formation of polyketones by condensation of dibenzo-crown ethers with long-chain dicarboxylic acids. See: Ueda, M.; Kano, T.; Twaragai, T.; Sugita, H. *Makromol. Chem., Rapid Commun.* **1985**, *6*, 847.

(4) A macrocyclic aromatic ether sulfone, with dicarboxylic acid functionality appended through short aliphatic chains, has been shown to give a low molecular weight ring−chain type polyamide on condensation with 4,4′-diaminodiphenylmethane. See: Rodewald, B.; Ritter, H. *Macromol. Rapid Commun.* **1997**, *18*, 817.

(5) Crystal data for **1**: $C_{38}H_{24}O_6{\cdot}2C_2HO_2F_3$, triclinic, $P\bar{1}$, $a = 8.086(1)$ Å, $b = 10.379(1)$ Å, $c = 12.125(1)$ Å, $\alpha = 106.90(1)°$, $\beta = 93.91(1)°$, $\gamma = 102.18(1)°$, $V = 942.6(2)$ Å^3, $M = 804.63$, $Z = 1$, $T = 293$ K, $R_1 = 0.0545$ for 2032 independent observed reflections [$F > 4\sigma(F_o)$]. Crystals of **1** were grown from a solution in dichlororomethane and trifluoroacetic acid. The solvating acid is retained in the crystal, where it is strongly hydrogen bonded to the carbonyl oxygen atoms. It has long been believed that the ability of strong acids to dissolve crystalline aromatic polyketones depends on protonation of the carbonyl groups, and the present study provides a rather elegant confirmation of this conjecture. Crystal data for **3**: $C_{76}H_{48}O_{12}{\cdot}2C_6H_{14}$, triclinic, $P\bar{1}$, $a = 10.192(1)$ Å, $b = 15.096(1)$ Å, $c = 22.057(2)$ Å, $\alpha = 86.42(1)°$, $\beta = 78.98(1)°$, $\gamma = 89.03(1)°$, $V = 3324.5(5)$ Å^3, $M = 1325.49$, $Z = 2$, $T = 293$ K, $R_1 = 0.0605$ for 6394 independent observed reflections [$F > 4\sigma(F_o)$].

(6) Crystal data for **5b**: $C_{52}H_{30}O_8Cl_2{\cdot}2C_2HO_2F_3{\cdot}C_6H_4Cl_2{\cdot}C_6H_{14}$, monoclinic, $C2/c$, $a = 28.856(6)$ Å, $b = 10.824(2)$ Å, $c = 23.421(5)$ Å, $\beta = 123.64(2)°$, $V = 6090(2)$ Å^3, $M = 1314.88$, $Z = 4$, $T = 183$ K, $R_1 = 0.0831$ for 2313 independent observed reflections [$F > 4\sigma(F_o)$].

(7) Alkylation of aromatic rings by chlorinated solvents during Friedel−Crafts polyaroylations has been reported. See: Clendinning, R. A.; Kelsey, D. R.; Botkin, J. H.; Winslow, P. A.; Youssefi, M.; Cotter, R. J.; Matzner, M.; Kwiatkowski, G. T. *Macromolecules* **1993**, *26*, 2361.

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