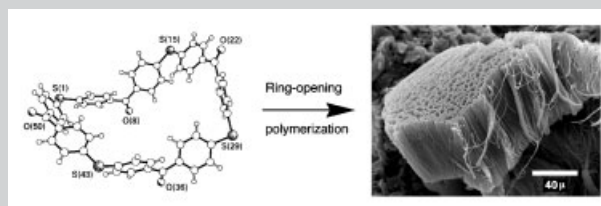


Summary: Spontaneous ring-opening polymerization of macrocyclic aromatic thioether ketones $[-1,4-SC_6H_4CO-C_6H_4-]_n$ ($n = 3$ and 4), in which the thioether linkages are *para* to the ketone, occurs during rapid, transient heating to $480\text{ }^\circ\text{C}$, to afford a soluble, semi-crystalline poly(thioether ketone) of high molar mass ($\eta_{inh} > 1.0\text{ dL} \cdot \text{g}^{-1}$). Corresponding macrocyclic ether ketones, and a macrocyclic thioether ether ketone in which the thioether linkage is *para* to the ether rather than to the ketone, show no evidence of polymerization under analogous conditions.



The uncatalysed ring-opening polymerization of macrocycle **1**, within the pores of an alumina microfiltration membrane, leads to formation of polymer **3** with the microstructure shown in the above scanning electron micrograph.

Spontaneous Ring-Opening Polymerization of Macrocyclic Aromatic Thioether Ketones under Transient High-Temperature Conditions

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Received: December 19, 2003; Revised: January 17, 2004; Accepted: January 22, 2004; DOI: 10.1002/marc.200300310

Keywords: crystal structures; macrocycles; microfabrication; poly(thioether ketone); ring-opening polymerization

Introduction

Commercially available high-performance polymers such as the aromatic polyimides,^[1] polysulfones,^[2] and polyketones,^[3] display outstanding thermo-oxidative stability and thermo-mechanical characteristics. However, their processability in microstructural applications is often limited by the high melt viscosities displayed by high-molar-mass materials of this type. As a result, there is currently intense interest in the development of ring-opening polymerization as an approach to reactive fabrication of these polymers from their homologous macrocyclic oligomers.^[4,5] The principal drawback of this approach lies in the presence of residual ionic material arising from the initiator required to achieve polymerization.^[4,5] In aromatic poly(ether ketone) systems, for example, this is generally a fluoride or phenoxide salt that initiates ring-opening polymerization by nucleophilic

attack at the activated ether linkages.^[4] For applications such as the formation of dielectric layers in electronic devices this ionic residue clearly represents a major disadvantage. However, a number of recent reports suggest that macrocycles containing the aromatic *thioether* unit can undergo uncatalysed, thermal ring-opening polymerization,^[6] although reactions of this type reported to date are relatively slow and generally afford at best only moderate conversion of macrocycle into polymer.^[6b,7] We now report that the macrocyclic aromatic oligomers $[-1,4-SC_6H_4COC_6H_4-]_n$ ($n = 3$ and 4), in which the thioether linkages are located specifically *para* to the **carbonyl** groups, polymerize very rapidly above their melting points, affording a soluble, semi-crystalline poly(thioether ketone) of high molar mass. In sharp contrast, an analogous macrocycle in which the thioether group is situated *para* to the **ether** linkages shows no evidence of polymerization under these conditions.

Experimental Part

Instrumentation and Materials

Proton and ^{13}C NMR data were recorded on Bruker DPX 250 and 400 MHz spectrometers with chemical shifts referenced to solvent resonances, and matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectra were obtained on a Micromass Tofspec instrument using dithranol as the matrix and sodium trifluoroacetate as a cationising agent. Differential scanning calorimetry (DSC) was carried out under nitrogen using a Mettler DSC-20 system (scanning rate $20\text{ }^\circ\text{C}\cdot\text{min}^{-1}$), and inherent viscosities (η_{inh}) were measured at $25\text{ }^\circ\text{C}$ on 0.1% polymer solutions in 98% H_2SO_4 using a Schott-Geräte CT-150 semi-automated viscometer. Scanning electron microscopy on gold-coated specimens was carried out using a Cambridge S360 digital microscope. Single crystal X-ray data were measured on a Siemens P4/RA diffractometer with graphite-monochromated $\text{Cu K}\alpha$ radiation. Alumina micro-filtration membranes (Anodisc, $0.1\text{ }\mu\text{m}$ nominal pore size) were obtained from Whatman. Starting materials were obtained from Aldrich and were used without further purification. The intermediate 4,4'-bis(4''-fluorobenzoyl)diphenyl ether was prepared according to the literature.^[8]

Synthesis and Characterization of Macrocycle 2

Condensation of sodium sulfide (7.41 g, 95.5 mmol) with 4,4'-dichlorobenzophenone (23.84 g, 95.00 mmol) was carried out in *N*-methylpyrrolidone (1 L) as described in ref.^[9] Precipitation into water (2 L) gave a cream solid which was filtered off, washed with water and methanol, dried and extracted with dichloromethane for 12 h. Evaporation of the extract gave a dark grey powder (5.20 g). Analysis by MALDI-TOF MS showed the product comprise a mixture of macrocyclic oligomers ranging from the cyclic dimer to the cyclic hexamer. Two recrystallizations of this material from chlorobenzene gave a mixture of macrocycles **1** and **2** in approximately a 3:2 mole ratio (2.83 g). A sample of this mixture (0.60 g) was subjected to column chromatography on silica gel with dichloromethane as eluent, affording the cyclic trimer **1** (0.22 g) and the previously unknown cyclic tetramer **2** (0.18 g).

Characterization Data for 2

M.p. $439\text{ }^\circ\text{C}$ (DSC).

IR (KBr) 1655 cm^{-1} (ν , C=O).

^1H NMR [$\text{CDCl}_3/\text{CH}_3\text{SO}_3\text{H}/\text{CF}_3\text{SO}_3\text{H}$ (10:2:1 vol./vol.), 250 MHz]: $\delta = 7.81$ (d, 16H), 7.56 (d, 16H).

^{13}C NMR [$\text{CDCl}_3/\text{CH}_3\text{SO}_3\text{H}/\text{CF}_3\text{SO}_3\text{H}$] (10:2:1 vol./vol.), 62.5 MHz]: $\delta = 200.7$, 143.3 , 135.5 , 131.7 , 130.2 .

MS (MALDI-TOF, dithranol matrix, CF_3COONa cationising agent): $m/z = 871$ [$\text{M} + \text{Na}$] $^+$.

Crystal Data for 2

$\text{C}_{52}\text{H}_{32}\text{O}_4\text{S}_4$, $M = 849.02$, monoclinic, space group $P2_1/c$, $a = 13.773(2)$, $b = 31.364(3)$, $c = 34.626(5)$ Å, $\beta = 96.26(1)^\circ$, $V = 14,869(3)$ Å 3 , $T = 293$ K, $Z = 12$ (3 independent molecules), $D_c = 1.138\text{ g}\cdot\text{cm}^{-3}$, $\mu(\text{Cu-K}\alpha) = 2.08\text{ mm}^{-1}$, $F(000) = 5280$, 20403 independent measured reflections,

$R_1 = 0.088$, $wR_2 = 0.232$ for 10978 independent observed reflections [$I > 2\sigma(I)$].

Synthesis and Characterization of Macrocycle 4

A solution of 4,4'-bis(4''-fluorobenzoyl)diphenyl ether (4.14 g, 10.0 mmol) and 4,4'-thiodiphenol (2.18 g, 10.0 mmol) in *N,N*-dimethylacetamide (DMAc, 100 mL) was added under nitrogen via a syringe pump (injection rate $2\text{ mL}\cdot\text{h}^{-1}$) to a stirred suspension of potassium carbonate (2.07 g, 15.00 mmol) in DMAc (400 mL) and toluene (200 mL) at reflux. The water generated was collected using a Dean-Stark trap. After addition was complete, the reaction was allowed to proceed for a further 12 h, the toluene was removed by distillation, and the solution was then cooled, filtered, and added to water (1 L) to give a cream precipitate that was filtered off, washed with water and methanol, and dried. Fractionation by column chromatography (dichloromethane eluent) afforded macrocycle **4** (0.88 g, 15% yield).

Characterization Data for 4

M.p. $439\text{ }^\circ\text{C}$ (DSC).

^1H NMR [$\text{CDCl}_3/\text{CF}_3\text{COOH}$ (5:1 vol./vol.), 250 MHz]: $\delta = 7.72$ (d, $J = 8.9$ Hz, 4H), 7.71 (d, $J = 8.8$ Hz, 4H), 7.53 (d, $J = 8.7$ Hz, 4H), 7.10 (d, $J = 8.7$ Hz, 4H), 7.07 (d, $J = 8.8$ Hz, 4H), 7.03 (d, $J = 8.9$ Hz, 4H).

^{13}C NMR [$\text{CDCl}_3/\text{CF}_3\text{COOH}$ (5:1 vol./vol.), 62.5 MHz]: $\delta = 200.3$, 163.7 , 162.6 , 155.1 , 134.9 , 134.1 , 133.3 , 133.2 , 133.0 , 131.1 , 122.1 , 119.9 , 116.8 .

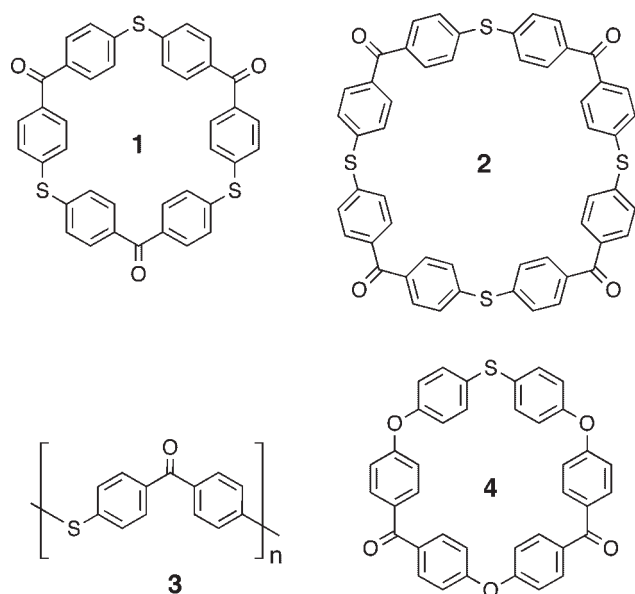
$(\text{C}_{38}\text{H}_{24}\text{O}_5\text{S})_n$ (592.14) $_n$: Calcd. C 77.02, H 4.05; Found C 77.03, H 4.02;

MS (CI) $m/z = 592.13$ [M] $^+$.

Results and Discussion

During an investigation of the macrocyclic thioether ketone **1** (Scheme 1), we discovered that the reported synthesis of this compound, involving reaction of 4,4'-dichlorobenzophenone with sodium sulfide under high dilution conditions,^[9] in fact yields an entire series of macrocyclic oligomers, $[-\text{S}-\text{Ar}-\text{CO}-\text{Ar}-]_x$ (Ar = 1,4-phenylene, $x = 3-6$) including not only the originally described cyclic trimer **1** but also the cyclic tetramer **2** (Scheme 1), as shown by MALDI-TOF MS. Both these latter macrocycles were isolated in high purity by column chromatography, and the structure of the novel macrocycle **2** was established by single crystal X-ray methods (Figure 1).

Thermal analysis of macrocycle **1** revealed unexpectedly complex behaviour (Figure 2). The sharp melting point ($451\text{ }^\circ\text{C}$) observed during an initial DSC scan from 90 to $480\text{ }^\circ\text{C}$ was not reproduced on the second scan. Instead, a glass transition at $150\text{ }^\circ\text{C}$ was observed, followed by a strong crystallization exotherm at $210\text{ }^\circ\text{C}$, and finally by a melting endotherm centred at $345\text{ }^\circ\text{C}$. These transitions closely parallel those reported for the high-molar-mass poly(thioether ketone) **3** (Scheme 1),^[10] homologous with



Scheme 1.

macrocycle **1**, and indeed inspection of a DSC sample after the initial scan revealed that the macrocycle had been converted into a tough polymeric product, fully soluble in strong acid media such as concentrated sulfuric acid. Measurements of inherent viscosity gave values of ca. $1 \text{ dL} \cdot \text{g}^{-1}$, confirming the formation of a high-molar-mass polymer comparable with commercial poly(ether ketones). Proton and ^{13}C NMR spectra of the ring-opened polymer in $\text{CDCl}_3/\text{CH}_3\text{SO}_3\text{H}/\text{CF}_3\text{SO}_3\text{H}$ as solvent were well-resolved and fully consistent with the formation of the linear all-*para* poly(thioether ketone) **3**. Remarkably, significant levels of residual macrocycle (i.e., >ca. 2 wt.-%) could not be detected by proton NMR analysis. Analogous results were obtained for macrocyclic thioether ketone **2**, which again afforded soluble, semi-crystalline polymer **3**. In each case, the total reaction time above the melting point of the macro-

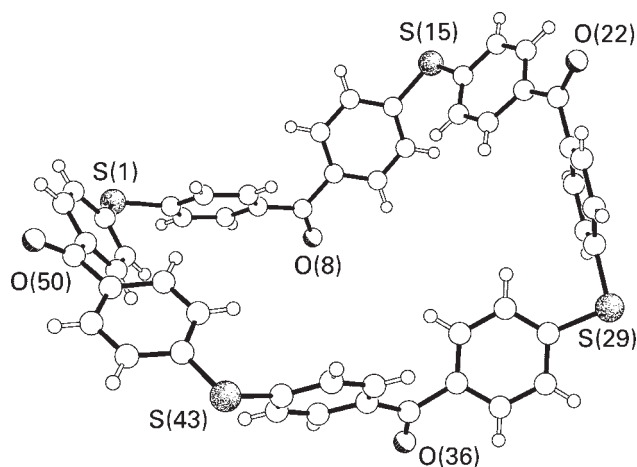
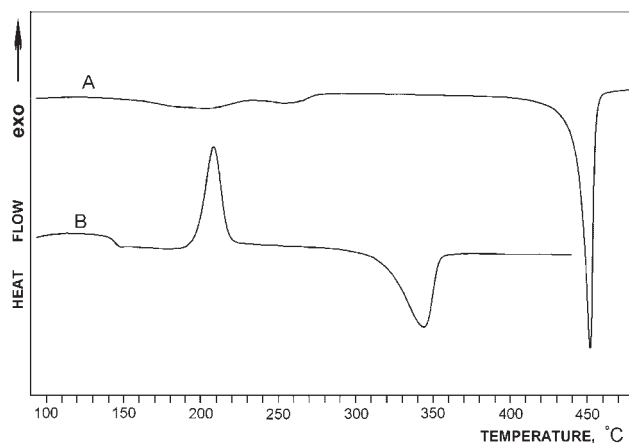
Figure 1. X-Ray structure of the macrocyclic tetramer **2**.

Figure 2. DSC heating scans ($15^\circ\text{C} \cdot \text{min}^{-1}$) for macrocycle **1**. Scan *A* shows melting of the macrocycle. Scan *B*, after rapid cooling, shows the glass, crystallization, and melting transitions of poly(thioether ketone) **3**.

cyclic oligomer (including cooling from 480 to 300°C) was no more than 3–4 min.

A series of control experiments was carried out to determine whether this type of very rapid, spontaneous ring-opening polymerization is unique to macrocycles containing the $[1,4\text{-SC}_6\text{H}_4\text{-CO}]$ unit. Indeed, the previously-reported^[11] macrocyclic ether ketone **5**, analogous to **1**, showed no indication whatsoever of polymerization on transient heating to 480°C , subsequent DSC scans simply reproducing the melting curve of the macrocycle. Perhaps more surprisingly, DSC analysis of macrocycle **4** – which contains diaryl thioether linkages, but now *para* to the ether rather than to the ketone – also gave little evidence of polymerization under the same conditions, the area under the oligomer melting curve being reduced in magnitude by no more than 10% on the second scan. Earlier reports of uncatalyzed polymerizations of aromatic macrocycles based on 1,4-ether-thioether linkages do, however, indicate relatively long timescales and incomplete conversions for these reactions, albeit when carried out at lower polymerization temperatures.^[6b]

Macrocyclic ether ketones are known to polymerize only by anionic mechanisms, whereas cyclic aromatic thioethers undergo ring-opening in the presence of both anionic^[5d] and free-radical^[5a,6b] initiators. It therefore seems probable that a free-radical mechanism is responsible for the spontaneous polymerization observed in the present work, although the observed acceleration of the reaction rate associated with the presence of electron-withdrawing carbonyl substituents *para* to the thioether linkage seems to suggest that charge-delocalisation from sulfur to carbonyl must play some role in the reaction. Further mechanistic work on this ring-opening polymerization is clearly required.

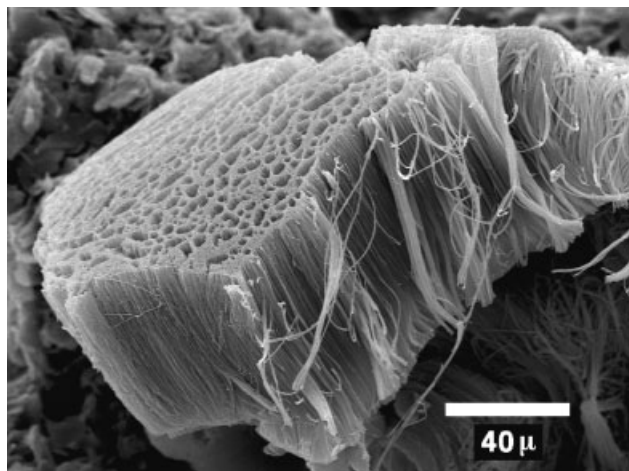


Figure 3. Scanning electron micrograph showing the fibrillar microstructure of polymer **3** formed by uncatalysed ring-opening polymerization of macrocycle **1** within the cylindrical pores of an alumina microfiltration membrane.

The potential of macrocyclic thioether ketones in polymer microfabrication was investigated by melt-phase polymerization within the cylindrical pores (nominal diameter 100 nm) of an alumina microfiltration membrane.^[12] A sample of macrocycle **1** was compressed to form a thin (ca., 0.1 mm) disc, which was placed in direct contact with the surface of the membrane. After transient heating to 480 °C, as described above, the alumina membrane was dissolved in aqueous sodium hydroxide and the structure of the polymeric residue was examined by scanning electron microscopy. A micrograph of the poly(thioether-ketone) resulting from ring-opening polymerization of macrocycle **1** is shown in Figure 3. The fibrillar microstructure, extending to the full thickness of the original alumina membrane (ca., 60 µm) provides strong evidence that the membrane pores have been completely filled by low-viscosity molten macrocycle, and the obvious flexibility of the resulting fibrils clearly demonstrate that, as in the non-templated polymerizations described above, the polymer formed is of high molecular weight. It should be emphasized that, even at these relatively high maximum polymerization and processing temperatures, there is no evidence for degradative side reactions, either of the polymer being fabricated or of the membrane template whose internal structure is successfully replicated. Qualitative observations also suggest that films of the poly(thioether-ketones) produced by ring-opening polymerization display excellent adhesive characteristics towards metal surfaces. Analogous effects have recently been reported for polymers produced by ring-opening polymerization of disulfide-linked aromatic macrocycles.^[13] In terms of durability, however, these latter materials (unlike the aromatic polythioethers obtained in the present work) would clearly reflect the limited thermal and chemical stability of the disulfide linkage.

Conclusion

The presence of ketone substituents *para* to aromatic thioether linkages greatly enhances the ability of macrocyclic systems to undergo spontaneous, uncatalysed ring-opening polymerization on transient heating to temperatures above 450 °C, relative to analogous macrocycles in which the thioether linkages are *para* to the ether. Ring-opening polymerization of macrocyclic thioether ketones enables rapid microfabrication of fibrillar polymer structures by an in-situ reaction within the cylindrical pores of an alumina microfiltration membrane.

Acknowledgement: We thank the EPSRC for research grants in support of this work (GR/M66554 and GR/M67087), DuPont for a European University Grant to H.M.C., and Universities UK for an Overseas Research Studentship to Z.Z.

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