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Synthesis of a Catechol-Based Poly(ether ether ketone) ("*o*-PEEK") by Classical Step-Growth Polymerization and by Entropically Driven Ring-Opening Polymerization of Macrocyclic Oligomers

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ABSTRACT: An amorphous, catechol-based analogue of PEEK ("*o*-PEEK") has been prepared by a classical step-growth polymerization reaction between catechol and 4,4′-difluorobenzophenone and shown to be readily soluble in a range of organic solvents. Copolymers with *p*-PEEK have been investigated, including an amorphous 50:50 composition and a semicrystalline though still organic-soluble material comprising 70% *p*-PEEK. *o*-PEEK has also been obtained by entropy-driven ring-opening polymerization of the macrocyclic oligomers (MCO's) formed by cyclo-condensation of catechol with 4,4′-difluorobenzophenone under pseudo-high-dilution conditions. The principal products of this latter reaction were the cyclic dimer **3a** (20 wt %), cyclic trimer **3b** (16%) cyclic tetramer **3c** (14%), cyclic pentamer **3d** (13%) and cyclic hexamer **3e** (12%). Macrocycles **3a**−**c** were isolated as pure compounds by gradient column chromatography, and the structures of the cyclic dimer **3a** and cyclic tetramer **3c** were analyzed by single-crystal X-ray diffraction. A mixture of MCO's, **3**, of similar composition, was obtained by cyclodepolymerization of high molar mass *o*-PEEK in dilute soluion.

1. Introduction

Many high performance polymers consist of aromatic rings linked together by ether, thioether, ketone, sulfone, amide, or imide groups.[1,2] One commercially important example is poly(ether ether ketone), **1** ("PEEK"),[3] a semicrystalline thermoplastic obtained by polycondensation of hydroquinone with 4,4′-difluorobenzophenone. This polymer combines outstanding mechanical properties with high thermal and chemical stability, and is relatively straightforward to synthesize.[3] However, its high melting point (ca. 335 °C) and insolubility in organic solvents, coupled with a high melt viscosity, mean that it can be difficult to process under certain conditions, for example in composite materials applications where rapid flow of molten polymer between high levels of reinforcing fiber is required. Such processing issues have focused attention on related homopolymers or copolymers that might be more easily processed because they have lower melting points and/or better solubilities. Polymers of this type that have so far been investigated include (i) those in which the ether:ketone ratio is varied,[4,5] (ii) those in which some of the aromatic rings are meta- rather than para-substituted,[6] and (iii) those containing substituents in a proportion of the aromatic rings.[7−9] There has however been no previous report of the simple homopolymer **2** (referred to in this paper as "*o*-PEEK") in which 1,2-phenylenedioxy units replace hydroquinone residues in the structure of PEEK itself, although several studies have been made of *polyimides* incorporating catechol units.[10] The present paper describes the synthesis, by classical step growth polymerization, of *o*-PEEK and two copolymers of *o*-PEEK with *p*-PEEK. [To avoid confusion, the polymer generally referred to as PEEK (**1**) will in this paper be referred to as *p*-PEEK, to clearly distinguish it from the new polymer *o*-PEEK (**2**).] We also describe a route to *o*-PEEK involving entropically driven ring-opening polymerization (ED-ROP) of macrocyclic oligomers (MCO's) **3,** synthesized either by cyclocondensation under pseudo-high-dilution conditions or by cyclo-depolymerization (CDP) of high molar mass *o*-PEEK (**2)** (see Chart 1).

Both ED-ROP and CDP exploit the ring−chain equilibrium that can be established, either thermally or in the presence of a suitable catalyst, between a homologous family of MCO's and the corresponding step growth linear polymer.[11−13] A feature of this type of equilibrium is that at *high* concentration it lies heavily in favor of the polymer, while at *low* concentration it shifts strongly in favor of the MCO's. For example, under solvent-free reaction conditions an equilibrated system would typically consist of ca. 98 wt % polymer and ca. 2% MCO's, while at high dilution it can easily comprise >90% of MCO's, and may consist almost exclusively of these.[14] Thus, if a *neat* macrocyclic aromatic ether-ketone, or a mixture of homologous macrocycles of this type, is allowed to undergo reversible ring-cleavage in the presence of a nucleophilic initiator, polymerization of the cyclic material will occur.[15−20]

Such ring-opening polymerizations (ROP's), which involve only a shuffling of linkages between the repeat units, have several potentially valuable features. For example, no volatiles or other byproducts are generated and, as the macrocycles are generally large enough to be strainless, little or no heat is evolved. The process is therefore an entropy-driven ring-opening polymerization (hereafter abbreviated as an ED-ROP). Conversely, when a *dilute* solution of high molar mass polymer is allowed to equilibrate by reversible chain-cleavage, then MCO's are formed in high yield, i.e., cyclo-depolymerization (CDP) occurs. It has been proposed that a combination of CDP and

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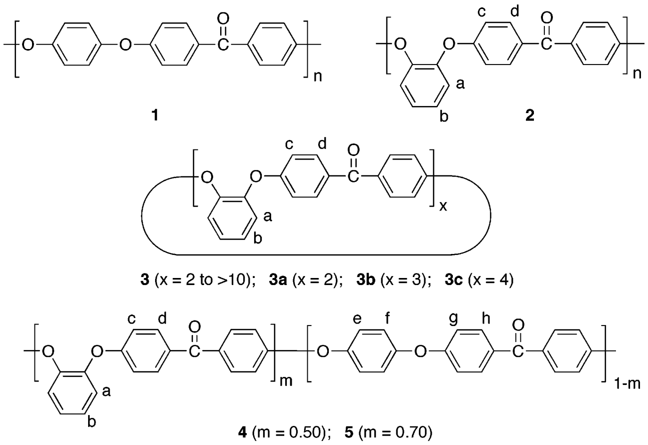
Chart 1. Linear and Macrocyclic Poly(ether ether ketone)s



ED-ROP could form the basis of a technique for recycling condensation polymers, and the two processes have been investigated for a number of different polymers of this type.[21−25]

2. Experimental Section

2.1. Methods and Materials. Techniques and instrumentation were as described in a previous paper.[25] Reagents and solvents were obtained from Aldrich and were used as received.

2.2. Synthesis of *o*-PEEK (2) by Step-Growth Polymerization. A mixture of 4,4′-difluorobenzophenone (8.00 g, 36.7 mmol), catechol (4.04 g, 36.7 mmol), and diphenyl sulfone (34.5 g) was heated gradually to 200 °C with stirring under nitrogen. Potassium carbonate (5.50 g, 39.8 mmol) was added slowly. After the reaction was stirred for 4 h at 200 °C, the temperature was raised to 320 °C and held there for a further 4 h. After cooling to room temperature, the solid product was dissolved in DMF (60 mL) and then precipitated by addition of the DMF solution to methanol (300 mL). The resulting polymer was filtered off and extracted first with hot methanol and then with boiling water, to remove diphenyl sulfone and potassium salts, respectively. The solid residue was finally dried at 70 °C in a vacuum oven to give polymer (**2**) as a white powder (9.92 g, 94% yield) with inherent viscosity (η_{inh}) 1.12 dL g^{-1} (NMP). Analysis by GPC (THF as solvent, polystyrene standards) gave M_n = 99 000 and M_w = 240 000; $\nu_{\max}$ (film) 1655 cm^{-1};^{1}H NMR (CDCl$_3$, 300 MHz) δ 7.75 (d, J = 8.8 Hz, 4H$_d$), 7.30 (m, 2H$_a$ and 2H$_b$) and 6.90 ppm (d, J = 8.8 Hz, 4H$_c$); ^{13}C NMR (CDCl$_3$, 75 MHz) δ ^{13}C NMR 194.02, 160.78, 146.55, 132.10, 131.97, 126.13, 122.64, and 116.11 ppm. Analysis by DSC showed T_g at 145 °C.

2.3. Copolymers of *o*-PEEK (2) and *p*-PEEK by Step-Growth Polymerization. Copolymer 4. A mixture of 4,4′-difluorobenzophenone (4.00 g, 18.3 mmol), catechol (1.00 g, 9.17 mmol), hydroquinone (1.00 g, 9.17 mmol), and diphenyl sulfone (17.50 g) was heated gradually to 200 °C with stirring under nitrogen; potassium carbonate (2.74 g, 20.0 mmol) was added. After the reaction was stirred for a further hour at 200 °C, the temperature was raised to 320 °C and held there for 3 h. After cooling to room temperature, the solid product was dissolved in dimethylacetamide (60 mL) and then precipitated in methanol (300 mL). The resulting solid was extracted with methanol and then boiling water and dried at 70 °C in a vacuum oven to give 4.92 g of copolymer **4** (93% yield). It had η_{inh} 0.70 dL/g (in sulfuric acid), and GPC indicated M_n = 8000 and M_w = 25 000; $\nu_{\max}$ (film) 1655 cm^{-1}. Analysis by DSC showed T_g at 130 °C.

Copolymer 5. A mixture of 4,4′-difluorobenzophenone (4.00 g, 18.3 mmol), catechol (0.60 g, 5.50 mmol), hydroquinone (1.41 g, 12.8 mmol), and diphenyl sulfone (17.50 g) was heated gradually to 200 °C with stirring under nitrogen; potassium carbonate (2.74 g, 20.0 mmol) was added and the polymerization was then conducted as described above. The white polymer (4.85 g, 92% yield) had η_{inh} 1.1 dL/g (in sulfuric acid) and GPC showed M_n = 18 000 and M_w = 43 000; $\nu_{\max}$ (film) 1656 cm^{-1}. Analysis by DSC showed T_g at 131 °C and T_m at 273 °C.

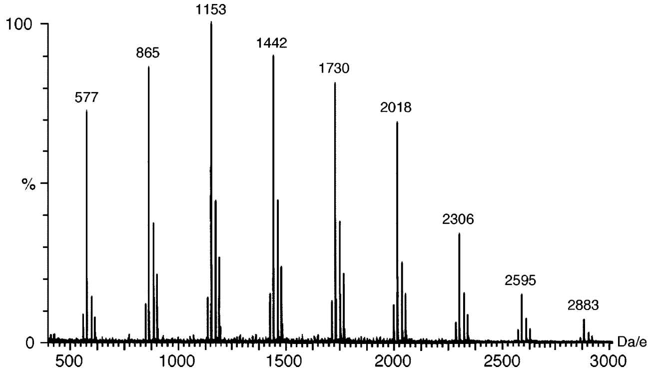


Figure 1. MALDI−TOF mass spectrum of the macrocyclic oligomers of *o*-PEEK obtained by cyclocondensation under pseudo-high-dilution conditions. Principal peaks correspond to [M + H]$^+$ for cyclic dimer (M = 576) to cyclic decamer. Spectrum obtained using dithranol as matrix.

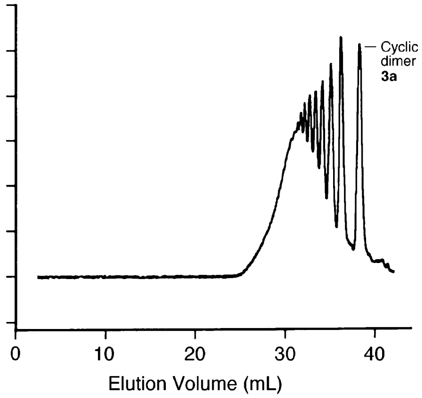


Figure 2. GPC trace (THF as eluent) of the macrocyclic oligomers of *o*-PEEK (**3**) obtained by cyclocondensation under pseudo-high-dilution conditions.

2.4. Cyclic Oligomers of *o*-PEEK by Pseudo-High-Dilution Synthesis. Cyclic oligomers of *o*-PEEK (**3**) were prepared by adding a solution of 4,4′-difluorobenzophenone (4.47 g, 20.5 mmol) and catechol (2.26 g, 20.5 mmol) in DMAc (100 mL) dropwise over a period of 5 h to a refluxing (145 °C) suspension of potassium carbonate (1.65 g, 12.0 mmol) in a mixture of toluene (40 mL) and DMAc (200 mL), under a nitrogen atmosphere. Water was continuously extracted with a Dean−Stark apparatus, and when addition was complete the temperature was raised to 155 °C by removal of toluene, and the mixture was refluxed for a further 15 h before cooling and filtering to remove insoluble salts. The product was recovered by evaporation to a leave ca. 60 mL of solution, followed by precipitation in water (300 mL) containing concentrated hydrochloric acid (10 mL). The product was filtered off and extracted with refluxing methanol to yield a white solid (5.50 g, 93%). This material (**3**) had iη_{inh} 0.17 dL g^{-1} (NMP); *m/z* (MALDI−TOF, dithranol) (100%, [M + H]$^+$) 577 (cyclic dimer), 865 (trimer), 1153 (tetramer), 1442 (pentamer), 1731(hexamer), 2018 (heptamer), 2306 (octamer) and 2595 (nonamer). Quantitative analysis by GPC showed that the final product comprised cyclic dimer **(3a)** 20%, trimer **(3b)** 16%, tetramer **(3c)** 14%, pentamer **(3d)** 13%, hexamer **(3e)** 12%, and higher homologues 25%.

2.5. Cyclic Oligomers of *o*-PEEK by Cyclo-Depolymerization. Polymer **2** (0.25 g, 0.86 mmol; η_{inh} = 1.12 dL g^{-1}) was heated under reflux in DMAc (50 mL) in the presence of cesium fluoride (0.065 g, 0.42 mmol). After 48 h, analysis by GPC (Figure 3) showed the solution to contain mainly cyclic material (**3**). The product was isolated by precipitation in acidified aqueous methanol (water 100 mL, MeOH 50 mL, concentrated HCl 5 mL) and was filtered off, washed with water and then methanol and dried under

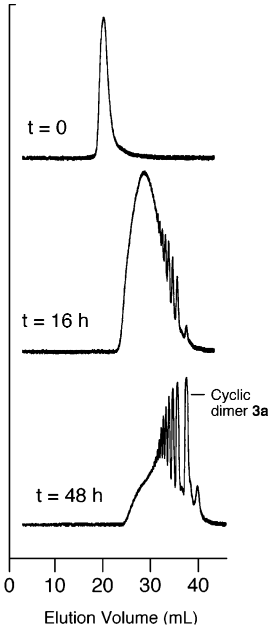


Figure 3. Cyclodepolymerization of *o*-PEEK (**3**) in dilute solution in DMAc, catalyzed by CsF. The GPC traces (THF as eluent) show progressive disappearance of high molar mass material and emergence of a series of sharp, discrete peaks corresponding to individual macrocycles, from cyclic dimer to cyclic decamer.

vacuum. The mixture had η_{inh} 0.17 dL g^{-1} (NMP); *m*/*z* (MALDI−TOF, dithranol) 577, 865, 1153, 1442, 1731, 2018, 2306, and 2595 corresponding to $[M + H]^+$ from cyclic dimer to nonamer. From GPC, the cyclic mixture contained cyclo-dimer **(3a)** 25%, trimer **(3b)** 17%, tetramer **(3c)** 15%, pentamer **(3d)** 10%, hexamer **(3e)** 9% and higher homologues 24%.

2.6. Isolation of Pure Cyclic Oligomers of *o*-PEEK from Pseudo-High-Dilution Synthesis. Individual cyclic oligomers were isolated by column chromatography over silica gel using a mixture of 99% dichloromethane and 1% acetonitrile as eluent. This gave pure cyclic dimer (15%), trimer (11%), and tetramer (9%) of *o*-PEEK, which were characterized as described below:

The cyclic *dimer* **3a** had mp 256 °C (by DSC); ν_{max} 1648 cm^{-3} (film); *m*/*z* (EI) [100%, $(M)^+$] 576; ^{1}H NMR ($CDCl_3$, 300 MHz) δ (ppm) 7.30 (m, 4H$_d$, 2H$_b$ and 2H$_a$), 6.60 (d, $J = 8.8$ Hz, 4H$_c$); ^{13}C NMR ($CDCl_3$, 75 MHz) δ (ppm) 192.03, 160.70, 146.34, 131.10, 131.12, 126.39, 125.15, and 115.59. Anal. Calcd for $(C_{19}H_{12}O_3)_2$: C, 79.15; H, 4.19. Found: C, 79.29; H, 4.43.

The cyclic *trimer* **3b** had mp 275 °C (by DSC); ν_{max} 1654 cm^{-3} (film); *m*/*z* (MALDI−TOF, dithranol) [100%, $(M + H)^+$] 866; ^{1}H NMR ($CDCl_3$, 300 Mz) δ (ppm) 7.60 (d, $J = 8.8$ Hz, 4H$_d$), 7.20 (m, 2H$_b$ and 2H$_a$) and 6.79 (d, $J = 8.8$ Hz, 4H$_c$); ^{13}C NMR ($CDCl_3$, 75 MHz) δ (ppm) 194.00, 160.08, 146.05, 132.07, 131.90, 126.15, 122.90, and 115.92. Anal. Calcd. for $(C_{19}H_{12}O_3)_3$: C, 79.15; H, 4.19. Found: C, 79.05; H, 4.50.

The cyclic *tetramer* **3c** had mp 338 °C (by DSC); ν_{max} 1651 cm^{-3} (film); *m*/*z* (MALDI−TOF, dithranol)) [100%, $(M + H)^+$] 1153; ^{1}H NMR ($CDCl_3$, 300 MHz) δ (ppm) 7.68 (d, $J = 8.8$, 4Hd), 7.30 (m, 2H$_b$ and 2H$_a$) and 6.90 (d, $J = 8.8$ Hz, 4H$_c$); ^{13}C NMR ($CDCl_3$, 75 MHz) δ (ppm) 193.84, 160.52, 146.20, 131.82, 130.69, 125.96, 122.82, and 115.77. Anal. Calcd for $(C_{19}H_{12}O_3)_4$: C, 79.15; H, 4.19. Found: C, 79.54; H, 4.47.

Crystal Data for Macrocycle 3a. $C_{38}H_{24}O_6 \cdot 1.8(CCl_4)0.2(CH_2Cl_2)$, MW 870.4, monoclinic, *P*2/c, $a = 35.831(4)$, $b = 6.160(1)$, $c = 17.063(1)$ Å, $\beta = 90.40(1)°$, $V = 3766.3(7)$ Å^3, $Z = 4$, $D_c = 1.535$ g cm^{-3}, μ(Cu Kα) = 56.14 cm^{-1}, $F(000) = 1766$, $T = 183(2)$ K. Independent reflections measured 5804 ($2\theta \leq 120°$), $R_1 = 0.058$, $wR_2 = 0.148$ for 3995 independent observed reflections [$F > 4\sigma(F)$].

Crystal Data for Macrocycle 3c. $C_{76}H_{48}O_{12}$, MW 1153.1, monoclinic, *C*2/c, $a = 24.637(5)$, $b = 14.634(1)$, $c = 17.525(3)$ Å, $\beta = 114.07(1)°$, $V = 5769(2)$ Å^3, $Z = 4$, (the molecule has crystallographic C_2 symmetry), $D_c = 1.328$ g cm^{-3}, μ(Cu Kα) = 7.29 cm^{-1}, $F(000) = 2400$, $T = 293$ K. Independent reflections measured 4360 ($2\theta \leq 124°$), $R_1 = 0.050$ $wR_2 = 0.126$ for 3228 independent observed reflections [$F > 4\sigma(F)$].

2.7. Ring-Opening Polymerization of *o*-PEEK Cyclic Oligomers. A finely powdered sample of the o-PEEK cyclic mixture [Table 2, entry 2] (0.20 g, 0.69 mmol) was ultrasonically dispersed in a methanol solution of CsF (4 mol % relative to the polymer repeat unit). The solvent was then removed in vacuo, and the residue was dried in a vacuum oven at 70 °C. A portion of the sample (ca. 20 mg) was encapsulated in a DSC crucible, heated under nitrogen to 320 °C (i.e., well above the melting point of the cyclic mixture at ca. 200 °C) and held at that temperature (320 °C) for 10 min. After cooling, the sample was reheated at 20 °C min^{-1} from 50 to 300 °C. The resulting DSC trace revealed a glass transition at 149 °C, and on removal from the DSC crucible the polymer was tough, impact resistant and pale brown in color. This material was fully soluble in DMAc, THF and chloroform, and GPC indicated $M_n = 44\,000$, $M_w = 83\,000$.

3. Results and Discussion

3.1. Synthesis of *o*-PEEK (2) and Copolymers 4 and 5 of *o*-PEEK and *p*-PEEK by Step Growth Polymerization. Polymer **2** and copolymers **4** and **5** were prepared by high-temperature nucleophilic polycondensation between catechol or catechol/hydroquinone mixtures and 4,4′-difluorobenzophenone in the presence of potassium carbonate. The resulting linear polymers were characterized by ^{1}H and ^{13}C NMR spectroscopy, gel permeation chromatography (GPC), differential scanning calorimetry (DSC), and thermogravimetric analysis (TGA). These results are summarized in Table 1, together with reference data determined for a commercial sample of *p*-PEEK (**1**).

The commercial sample of *p*-PEEK (**1**) (Table 1, entry 1) was insoluble in chloroform, DMAc, and all other organic solvents unless they contained trifluoroacetic acid or a similarly strong protic acid. This polymer showed a T_g of 143 °C and a T_m of 335 °C by DSC, in good agreement with literature data.[2] Analysis by TGA showed 50% weight loss up to 800 °C. In sharp contrast, the new polymer *o*-PEEK (**2**), (Table 1, entry 2), obtained here at high molar mass and in 94% yield, was readily soluble in a wide range of organic solvents, including dichloromethane, THF and DMAc. Its ^{1}H and ^{13}C NMR spectra were fully consistent with the expected structure, and by GPC it had M_n 99 000 and M_w 240,000, corresponding to a polydispersity of 2.4. It had an inherent viscosity of 1.12 dL g^{-1} in NMP. In keeping with the ready solubilty of *o*-PEEK, thermal analysis by DSC showed this polymer to be fully amorphous, with a T_g of 145 °C. Thermogravimetric analysis under nitrogen showed the onset of weight loss occurring at around 480 °C, and by 800 °C it had lost ca. 52% of its mass.

The two copolymers of *o*-PEEK and *p*-PEEK (**4** and **5**, Table 1, entries 3 and 4) had slightly lower T_g values than either of the homopolymers, perhaps as a result of their relatively low molecular weights. Copolymer **4**, containing equal proportions of *o*- and *p*-PEEK units, was fully amorphous, but copolymer **5**, with only 30% of *o*-PEEK units, had some degree of crystallinity, with a melting point of 273 °C, ca. 62 °C lower than that of *p*-PEEK. Both copolymers dissolved in amide-type solvents (DMF, DMAc, and NMP) on heating, and in chlorinated solvents (dichloromethane, chloroform) containing 5% trifluoroacetic acid.

3.2. Synthesis, Characterization and Entropy-Driven Ring-Opening Polymerization of Macrocyclic Oligomers of *o*-PEEK (3). An alternative route to *o*-PEEK would involve the ED-ROP of its macrocyclic oligomers. As no volatiles and little or no heat are evolved during ED-ROP, and MCO's have very

Table 1. Synthesis of *o*-PEEK and Its Copolymers with *p*-PEEK via Classical, Step-Growth Polycondensation at 320 °C in Diphenyl Sulfone as Solvent

entry	polymer	yield (%)	T_g, °C	T_m, °C	mol wt M_w	mol wt M_n	weight loss (%) at 800 °C (N_2)
1[a]	**1**		143	335			50
2[b]	**2**	94	145	amorphous	240 000	99 000	52
3[c]	**4**	92	130	amorphous	25 000	8000	57
4[d]	**5**	92	131	273	43 000	18 000	56

[a] PEEK-450P, from Victrex PLC. [b] *o*-PEEK. [c] 50:50 ortho:para. [d] 30:70 ortho:para.

Table 2. Synthesis of *o*-PEEK Macrocyclic Oligomers 3

reaction	yield, %	η_{inh}, dL/g[a]	highest cyclic identified[b]	composition of product[c] % of individual cyclic *n*-mers by weight: $n = 2$	$n = 3$	$n = 4$	$n = 5$	$n = 6$	$n = 7$	$n = 8$	others[d]
CDP[e]	90	0.18	$n = 9$	25[f]	17[f]	15[f]	10	9	7	5	12
HD[g]	93	0.17	$n = 9$	20[f]	16[f]	14[f]	13	12	8	6	11

[a] Inherent viscosity of the cyclic mixture (in DMAc). [b] Samples of products were studied by MALDI−TOF MS; peaks were seen for $n = 2$ up to the values given. [c] By GPC analysis. [d] Higher homologues. [e] CDP of polymer **2**. [f] A pure sample of this cyclic was isolated and fully characterized. [g] Pseudo-high-dilution synthesis from 4,4-difluorobenzophenone and catechol.

much lower melt-viscosities than their corresponding high molar mass polymers,[26] ED-ROP is a potentially valuable method for the preparation of high performance polymer composites[27] and for reaction injection molding (RIM) of highly detailed and/or microscale moldings.[28] We have therefore investigated the synthesis of *o*-PEEK by ED-ROP. Two alternative routes to the required cyclic oligomers were explored in this work: cyclocondensation of catechol with 4,4′-difluorobenzophenone under pseudo-high-dilution conditions, and cyclodepolymerization of high-MW *o*-PEEK.

3.3. Macrocyclic Oligomers 3 by Pseudo-High Dilution Synthesis. A dilute, equimolar solution of 4,4′-difluorobenzophenone and catechol in DMAc was added dropwise over 5 h to a suspension of potassium carbonate in DMAc and toluene at 150 °C, with continuous azeotropic removal of water. This gave MCO's **3** in 93% yield. They were soluble in a wide range of organic solvents, and their ^{1}H and ^{13}C NMR spectra agreed well with the expected structures: for example there was no evidence of end groups. Analysis by MALDI−TOF MS confirmed the cyclic nature of the oligomers and indicated that the mixture consisted of macrocycles containing from 2 up to at least 10 repeat units (Figure 1). Analysis by GPC revealed a series of homologous MCO's (Figure 2) with the cyclic dimer **3a** as the major product. This GPC analysis was confirmed when pure, well-characterized samples of the cyclic dimer (**3a**) and cyclic tetramer (**3c**) were isolated as described below and were used to calibrate the GPC trace. The overall composition of the mixed macrocylic product is summarized in Table 2.

3.4. Preparation of Cyclic Oligomers 3 by Cyclo-Depolymerization. As noted above, the combination of CDP with ED-ROP is of interest as a potential method for recycling high value step-growth polymers. Accordingly, it was of interest to investigate the CDP of *o*-PEEK. This was achieved using a 0.5% w/v solution of *o*-PEEK (**2**) in DMAc at 230 °C, with ring−chain equilibrium being established via reversible nucleophilic cleavage of the ether linkages catalyzed by cesium fluoride. The progress of the reaction was conveniently monitored by GPC. After 48 h the initial, broad, high-MW peak associated with linear polymer (**2**) was entirely replaced by a series of sharp, low-MW peaks due to discrete oligomers (Figure 3), which were subsequently isolated in 94% yield and characterized. Analysis by MALDI−TOF MS indicated that the product consisted of a family of homologous *macrocyclic* oligomers (**3**), with ring-sizes from the dimer up to at least the decamer. The ^{1}H and ^{13}C NMR spectra also agreed well with the expected cyclic structures. Analysis by GPC showed that the proportions of the different MCO's were qualitatively in agreement with the theory of Jacobson and Stockmayer,[29] which at its simplest predicts that, if the rings are strainless, then at equilibrium (as is generally the case in cyclo-depolymerization) they will be present in decreasing proportions as the rings become larger. S*trained* rings however will be present only at a very low level, if indeed at all. Although MCO's produced by pseudo-high-dilution synthesis are initially formed under kinetic control, they may slowly equilibrate during the reaction, as a result of reversible ring-opening by fluoride or phenoxide ions. In any case, it is known that the proportions of kinetic and thermodynamic products in this situation are often,[26] though not always,[30] rather similar.

3.5. Isolation and Characterization of the Cyclic Dimer (3a), Trimer (3b), and Tetramer (3c): Samples of pure individual oligomers were isolated to allow calibration of the GPC (see above). The mixed cyclic fraction **3** was separated by gradient elution chromatography over silica gel, allowing the isolation of pure cyclic dimer (**3a**), trimer (**3b**), and tetramer (**3c**). These are all crystalline and melt sharply at 255, 275, and 338 °C, respectively. It should however be noted that the *mixed*-macrocyclic fraction (**3**) is amorphous and begins to flow freely at ca. 200 °C. This effect has been observed with other macrocyclic oligomers,[26,30] and, in some respects makes the mixture of MCO's more attractive as a feedstock for ED-ROP than the pure, isolated macrocycles.

The three isolated macrocycles (**3a**−**3c**) were characterized by FT-IR and by ^{1}H and ^{13}C NMR spectroscopies, by FAB mass spectrometry, and by elemental analysis. Their ^{1}H NMR spectra varied significantly as a function of ring size, so that for example, in the cyclo-dimer **(3a)** the resonance arising from the protons (H_d) ortho to the carbonyl groups appeared ca. 0.4 ppm upfield relative to those of the larger ring-size macrocycles (Figure 4). Such a shift could well result from these protons lying within the ring-current shielding zones of aromatic rings diametrically opposite them within the macrocycle, and this effect would clearly be most pronounced for the smallest and least flexible macrocycle of the series.

In the cases of the cyclic dimer **(3a)** and tetramer (**3c**), single crystals suitable for X-ray crystallography were obtained, and the molecular structures of **3a** and **3c** are shown in Figures 5 and 6, respectively. The cyclic dimer **3a** adopts a narrow, boat-shaped conformation (Figure 5) in which the two catechol residues lie on the same side of the molecule, roughly orthogonal

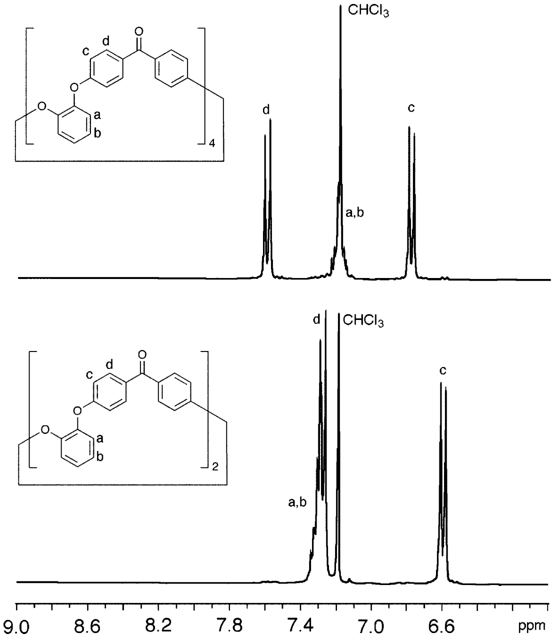


Figure 4. ^{1}H NMR spectra ($CDCl_3$, 300 MHz) of the cyclic dimer (**3a**) and cyclic tetramer (**3c**) of *o*-PEEK, showing the upfield shift of resonances in the dimer ascribed to mutual transannular ring-current shielding.

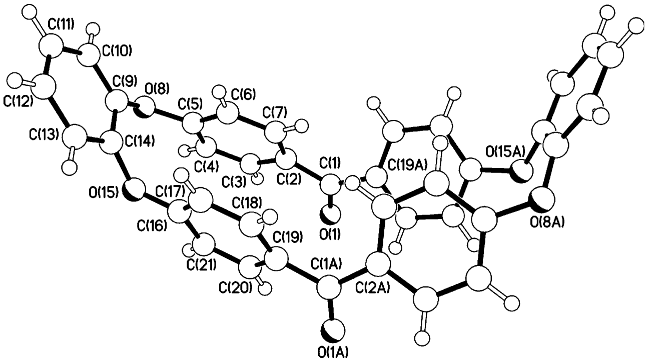


Figure 5. X-ray structure of the cyclic dimer (**3a**) of *o*-PEEK.

to their adjacent aromatic rings. The four "ether−ketone" rings are stacked very closely and almost parallel to one another in symmetry-related pairs (the molecule has a crystallographic 2-fold axis), with several carbon atoms separated by much less than van der Waals contact distances (ca. 3.4 Å for aromatic rings). Carbon−carbon contacts as short as 3.11 Å [C(6)−C(16)] and 3.26 Å [C(5)−C(16)] are observed, and the centroid-centroid separation between the adjacent rings C(2)−C(7) and C(16)−C(21) is 3.73 Å. Bond angles at ether and ketone are essentially unstrained [C(5)−O(8)−C(9) = 120°; C(14)−O(15)−C(16) = 123°; C(2)−C(1)−C(19a) = 123°). The overall structure of macrocycle **3a** is not dissimilar to those of several published macrocylic ether-ketone oligomers,[27] except that in this molecule, as noted above, a series of unusually close intermolecular contacts result from the presence of the ortho-linking catechol residues. This "self-stacked" conformation is entirely consistent with the proposal (above) that the marked upfield shifts of ^{1}H NMR resonances in this, the smallest macrocycle of *o*-PEEK, may result from transannular ring-current shielding effects.

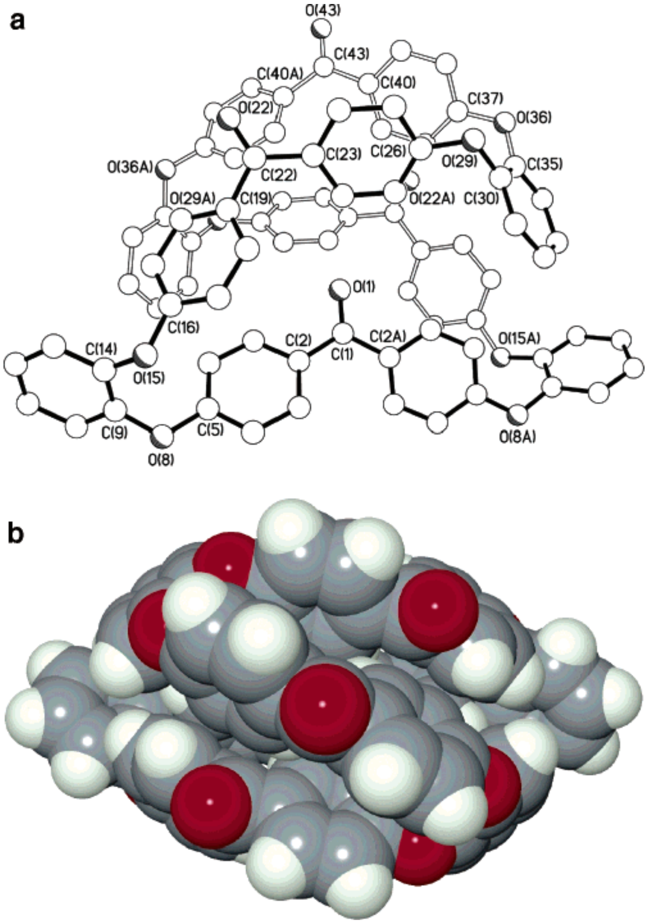


Figure 6. (a) X-ray structure of a single molecule of the cyclic tetramer of *o*-PEEK. Shaded and unshaded bonds are used to indicate perspective. (b) Single molecule of the cyclic tetramer of *o*-PEEK (oxygen atoms in red) viewed down the 2-fold axis, showing the tightly folded relationship between monomer residues.

The cyclic tetramer **3c** adopts a highly convoluted and quite unprecedented structure (Figure 6) in which the ortho-substituted catechol residues force the chain to wind sharply back and forth across the molecule, leading to a tightly folded conformation somewhat resembling a small globular protein. Despite its irregular appearance in Figure 6a, this macrocycle (like cyclodimer **3a**) does in fact have a crystallographic 2-fold axis, and this is brought out in the space-filling representation shown in Figure 6b, which shows a projection down the two carbonyl bonds lying on this axis. Overall, the ether−ketone rings are a little less closely packed than in cyclic dimer **3a** (presumably due to to the greater conformational freedom of the tetramer relative to the dimer) but there are still a small number of close inter-ring contacts, including C(6)−C(16) at 3.18 Å, C(26)−C(37) at 3.35 Å, and C(5)−C(16) at 3.42 Å.

3.6. Entropically Driven ROP of Macrocyclic Precursors to *o*-PEEK.

Entropically driven ROP typically involves estab-

Table 3. Ring-Opening Polymerization of *o*-PEEK Macrocyclic Oligomers 3 and 3a

starting material	catalyst, mol %	T_g (°C)	M_w[c]	M_n[c]
cyclic dimer of *o*-PEEK (**3a**)[a]	CsF, 3%	144	110 000[d]	47 000[d]
macrocyclic *o*-PEEK fraction (**3**)[b]	CsF, 4%	149	83 000	44 000
macrocyclic *o*-PEEK fraction (**3**)[b]	CsSPhCOPhSCs, 3%	157	120 000	65 000
macrocyclic *o*-PEEK fraction (**3**)[b]	CsOPhCOPh, 4%	161	640 000	250 000

[a] ROP carried out at 350 °C for 15 min. [b] ROP carried out at 320 °C for 10 min. [c] Molecular weights measured by GPC relative to polystyrene standards, with THF as eluent. [d] Final polymer not fully soluble in THF

lishing ring–chain equilibrium in a *neat* cyclic oligomer or mixture of MCO's. Clearly the synthesis of linear polymers from MCO's requires the introduction of end groups, and these are often derived from the catalyst used to establish the equilibrium. To facilitate full equilibration, reaction conditions should be used that allow molecular mobility to be maintained throughout the reaction. Thus, in the present case, the reaction temperature would need to be higher (preferably much higher) than the T_g of *o*-PEEK, i.e., 145 °C.

Several ED-ROPs were carried out, as shown Table 3. Polymerization of the pure macrocyclic dimer **3a** at 350 °C, with cesium fluoride as catalyst led to formation of a dark, partially cross-linked material, but lower-temperature polymerizations of the mixed-macrocycle fraction **3** were much more successful. The finely powdered MCO's were ultrasonically dispersed into a methanol solution of the catalyst and the solvent was then evaporated and the residue dried in a vacuum oven. Polymerizations were carried out by heating to 320 °C in the DSC instrument under nitrogen for 10 min and, after cooling, the samples were remeasured over the range 50 to 300 °C. Glass transition temperatures corresponded closely to the T_g of *o*-PEEK (**1**) synthesized by nucleophilic polycondensation and, on removal from the DSC crucible, the final polymers were found to be tough, impact resistant, pale brown in color, and fully soluble in organic solvents including chloroform, DMAc, and THF. Of particular note was the polymer produced using the cesium salt of 4-hydroxybenzophenone as catalyst. This polymer proved to be of extraordinarily high molecular weight ($M_w > 600\,000$) yet was still completely soluble.

4. Conclusions

The catechol-based analogue of PEEK ("*o*-PEEK") may be prepared by step growth polymerization between catechol and 4,4′-difluorobenzophenone. This amorphous polymer has T_g in the range 143–161 °C (depending on MW) and is readily soluble in a range of organic solvents. Copolymers containing up to 50% of *p*-PEEK monomer units are also amorphous, but at 70% *p*-PEEK the copolymer has a degree of crystallinity although it is still soluble in organic solvents. *o*-PEEK can also be prepared efficiently by ED-ROP of macrocyclic oligomers obtained by condensation of catechol and 4,4′-difluorobenzophenone under pseudo-high-dilution conditions. Macrocyclic components of the product include the cyclic dimer, (20%), cyclic trimer **3b** (16%) and cyclic tetramer **3c** (14%), which were isolated as pure compounds by gradient chromatography. A mixture of MCO's **3** of similar composition was obtained by CDP of high molar mass *o*-PEEK. The crystal and molecular structures of the cyclic dimer and cyclic tetramer were determined by single crystal X-ray diffraction, the latter showing a tightly folded, protein-like conformation with virtually no free space within the macrocycle.

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Supporting Information Available: Full crystallographic data in CIF format and figures showing thermal ellipsoid plots for the X-ray structures of macrocycles **3a** and **3c**. This material is available free of charge via the Internet at http://pubs.acs.org.

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