Enthalpy-Driven Ring-Opening Polymerization of Highly Strained Macrocyclic Biaryl-Ether-Ketones

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ABSTRACT: Highly strained macrocyclic ether−ketones obtained by nickel-catalyzed cyclization of linear precursor oligomers undergo ring-opening polymerization via ether exchange in the presence of nucleophilic initiators such as fluoride or phenoxide anions. Strain enthapies of these macrocycles, from DSC analyses of their exothermic ring-opening polymerization are in the range 50−90 kJ mol^{-1}. Melt-phase polymerization generally affords slightly cross-linked materials, but solution-phase polymerization at high macrocycle concentrations gives fully soluble, high molar mass polymers with inherent viscosities of up to 1.78 dL g^{-1}. Sequence-analysis of the resulting polymers by ^{13}C NMR shows that alternating or random monomer sequences may be obtained, depending on whether one or both aromatic rings adjacent to the ether linkages are activated toward nucleophilic attack.

1. Introduction

As outlined in the preceding paper,[1] there is considerable current interest in the synthesis of high-performance engineering thermoplastics by ring-opening polymerization of macrocyclic oligomers.[2] Such oligomers characteristically exhibit very low melt viscosities and liberate no volatile (or indeed any other) coproducts during polymerization, so that they are attractive precursors for composite materials production and for reactive fabrication of high performance polymers in general.[3] Many polymerizable aromatic macrocycles have been synthesized by nucleophilic cyclo-condensation of ketone- or sulfone-activated dihaloarenes with bis(phenols), and the resulting macrocyclic ether−ketones and ether−sulfones have been polymerized by nucleophile-initiated ether exchange.[2] Macrocyclic aromatic ethers produced by nucleophilic aromatic etherification are almost invariably strain-free, as a result of the reversibility of the S_NAr reaction, and their ring-opening polymerization thus depends almost entirely on entropic effects.[4] We have however shown in the preceding paper,[1] and in earlier communications,[5,6] that nickel(0)-catalyzed cyclization of haloarene-terminated oligomers allows the creation of highly strained biaryl-containing macrocyclic aromatic ether−ketones and ether−sulfones. In the present paper we describe the *enthalpy-driven* ring-opening polymerization of such macrocycles, both in the melt and in solution, and show that the high levels of strain evident in their structures can be determined semiquantitatively in terms of the enthalpy released during ring-opening polymerization.

2. Experimental Section

2.1. Materials and Instrumentation. Macrocyclic oligomers **1**, **2**, **3**, and **4** were synthesized as described in the preceding paper,[1] and were dried at 200 °C under vacuum for 24 h to ensure complete removal of solvent of crystallization. The monomers 4,4′-diphenoxydiphenyl sulfone,[7] 2,2-bis(4-phenoxyphenyl)hexafluoropropane,[8] and 2,8-diphenoxydibenzofuran[7] were prepared according to the literature. Other reagents and solvents were obtained from Aldrich and, unless stated otherwise, were used as received. Trifluoromethanesulfonic acid was distilled under dry nitrogen before use. The initiators di-potassium 4,4′-biphenoxide and potassium 4-benzoylphenoxide were prepared according to the literature.[9] Instrumentation was as described in the preceding paper. Solution viscometry was carried out at 25 °C on 0.1% polymer solutions in 98% sulfuric acid, using a Schott-Geräte semi-automated Ubbelohde viscometer, and NMR spectra were recorded using solutions in a mixture of CD_2Cl_2 and methanesulfonic acid (%:1 v/v). Analytical HPLC was carried out using a Hichrom ZSIL-1307 column, a P-E Series-200 LC pump and P-E 235C diode array UV detector operating at 255 nm. Assignments of ^1H NMR signals, where given, refer to the labeled structures shown in Schemes 1−4.

2.2. Melt-Phase Ring-Opening Polymerization of Macrocyclic Ether—Ketone 3. Macrocycle **3** (100 mg) was dissolved in dichloromethane (20 mL), and a solution of cesium fluoride (3.0 mg) in methanol (5 mL) was added. The solution was evaporated, and the residual powder was dried at 140 °C under vacuum overnight. A sample of the dried powder was pressed into a pellet (10 mg) and placed in a DSC crucible. The sample was then heated at a rate of 10 °C min^{-1}, under nitrogen, to 373 °C (i.e., 20 °C above the melting point of the macrocycle) and the melting endotherm and polymerization exotherm were monitored. After 5 min, the sample was cooled to 50 °C and reheated to 360 °C to measure the glass transition temperature of the resulting polymer (**7a**). Analogous polymerizations of macrocycles **1**, **2**, and **4** afforded polymers **5a**, **6a**, and **8a** respectively, as detailed in Table 1.

2.3. Ring-Opening Polymerization of 3 in *N*-Methylpyrrolidone (NMP). A solution of macrocycle **3** (100 mg, 0.17 mmol) and potassium 4,4-biphenoxide (0.89 mg, 3.4×10^{-3} mmol) in NMP (0.34 mL) was stirred at 200 °C for 2 h under nitrogen. The resulting viscous solution was added dropwise to stirred methanol (10 mL), and the polymer beads so obtained (**7b**) were extracted with ethanol (2×20 mL) at reflux and dried under vacuum at 80 °C.

Polymer 7b. $T_g = 252$ °C; $\eta_{inh} = 1.01$ dL g^{-1}. ^1H NMR (CD_2Cl_2:$MeSO_3H$ 5:1, 250 MHz), δ (ppm): 8.24 (d, $J = 8.5$ Hz, $4H_b$), 8.14 (br, $4H_a$ and $4H_c$), 7.89 (br, $2H_g$), 7.79 (d, $J = 8.9$ Hz, $2H_f$), 7.40 (d, $J = 8.9$ Hz, $2H_e$), 7.31 (d, $J = 8.5$ Hz, $4H_d$). ^{13}C NMR (CD_2Cl_2:$MeSO_3H$ 5:1, 100 MHz), δ (ppm): 201.7, 170.5, 154.7, 148.7, 147.4, 140.4, 134.9, 130.8, 128.6, 125.2, 123.6, 121.2, 118.1, 113.7.

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Table 1. Enthalpies of Polymerization for Macrocycles 1−4[a]

macrocycle (T_m (°C))[b]	initiator	ΔH (kJ mol^{-1}) 1 wt % initiator	2 wt % initiator	3 wt % initiator	5 wt % initiator	10 wt % initiator
1 (354)	KBZ[c]				56	55
	CsF				52	55
2 (387)	KBZ[c]				58	
	CsF				58	63
3 (353)	KBZ[c]	83	85	81		
	CsF	77	77	83		
4 (410)	KBZ[c]					
	CsF	88	87	86		

[a] Measured by DSC, at a heating rate of 10 °C min^{-1}. [b] The maximum temperature reached during each heating scan was 20 °C above T_m. [c] KBZ = potassium 4-benzoylphenoxide.

2.4. Ring-Opening Polymerization of Macrocycle 1 in Diphenyl Sulfone. A mixture of macrocycle **1** (0.486 g, 0.8 mmol), dipotassium 4,4′-biphenoxide (4.5 mg, 0.017 mmol), and diphenyl sulfone (1.62 g) was charged to a reaction tube equipped with a mechanical stirrer and a nitrogen inlet. The reaction mixture was placed in a preheated silicone oil bath at 250 °C, stirred for 2.5 h, and then cooled to room temperature. The solid was crushed to a coarse powder, refluxed with methanol (2 × 100 mL) and then with water (2 × 100 mL), and finally washed with methanol and dried at 80 °C under vacuum to give polymer **5b** as a white powder. Analogous polymerizations of macrocycles **2** and **4** gave polymers **6b** and **8b**, respectively.

Polymer 5b. T_g = 221 °C; η_{inh} = 1.32 dL g^{-1}. ^{1}H NMR (CD_2Cl_2:$MeSO_3H$ 5:1, 250 MHz), δ (ppm): 8.33 (m), 8.26 (m), 8.20 (br), 8.11 (d, J = 8.4 Hz), 7.85 (dd), 7.77 (dd), 7.70 (br d), 7.62 (dd), 7.50 (br), 7.40 (m). ^{13}C NMR (CD_2Cl_2:$MeSO_3H$ 5:1, 100 MHz), δ (ppm): 203.4, 202.9, 167.2, 164.3, 160.2, 160.0, 158.2, 158.1, 147.5, 147.3, 139.7, 139.3, 138.7, 136.9, 136.7, 135.2, 135.0, 134.8, 134.5, 131.7, 131.0, 130.5, 130.3, 130.2, 130.1, 129.9, 128.6, 127.4, 127.2, 125.3, 121.7, 120.3, 120.0, 119.0.

Polymer 6b. T_g = 188 °C; η_{inh} = 1.15 dL g^{-1}. ^{1}H NMR (CD_2Cl_2:$MeSO_3H$ 5:1, 250 MHz), δ (ppm): 8.26 (d, J = 8.6 Hz, $4H_b$), 8.16 (br s, $4H_c$ and $4H_a$), 7.61 (d, J = 8.1 Hz, $4H_f$), 7.34 (d, J = 8.1 Hz, $4H_d$ and $4H_e$). ^{13}C NMR (CD_2Cl_2:$MeSO_3H$ 5:1, 100 MHz), δ (ppm): 202.2, 169.0, 153.8, 147.5, 140.3, 135.1, 132.4, 130.8, 130.6, 128.6, 124.1, 120.9, 118.4.

Polymer 8b. T_g = 241 °C; η_{inh} = 1.78 dL g^{-1}. ^{1}H NMR (CD_2Cl_2:$MeSO_3H$ 5:1, 250 MHz), δ (ppm): 8.90 (m, $2H_f$), 8.39 (d, $4H_a$, $4H_b$ and $4H_c$), 7.80 (m, $4H_d$, $2H_e$ and $2H_g$). ^{13}C NMR (CD_2Cl_2: $MeSO_3H$ 1:5, 100 MHz), δ (ppm): 202.0, 201.7, 173.5, 173.2, 172.9, 164.2, 163.9, 162.9, 162.7, 161.2, 161.1, 158.8, 158.6, 158.4, 145.7, 137.1, 136.5, 133.3, 133.2, 130.1, 129.7, 128.1, 127.7, 127.5, 127.3, 126.8, 126.6, 125.4, 119.1, 118.6, 118.2, 110.2, 109.6, 105.4.

2.5. Electrophilic Polycondensations in Trifluoromethanesulfonic Acid (General Procedure). Trifluoromethanesulfonic acid (5 mL) was added to a mixture of the aromatic diether **9**, **10**, or **11** (1.02 mmol) and biphenyl-4,4′-dicarboxylic acid (0.242 g, 1 mmol) under dry nitrogen. The resulting dark red, clear solution quickly became viscous and was stirred at room temperature for 26 h. The solution was then run dropwise into water (100 mL) with vigorous stirring. The resulting pink beads of polymer were stirred in boiling water for 1 h, filtered off, and then stirred with sodium hydroxide in 1:1 aqueous ethanol (0.25 M, 200 mL) for 1 h at room temperature. The now pale-cream polymer (**5c**, **6c**, or **7c** respectively) was filtered off, washed with water, refluxed with ethanol (100 mL) for 0.5 h, filtered again, and dried under vacuum.

Polymer 5c (0.60 g, 92% Yield). T_g = 212 °C; η_{inh} = 0.73 dL g^{-1}. ^{1}H NMR (CD_2Cl_2:$MeSO_3H$ 5:1, 250 MHz), δ (ppm): 8.23 (d, J = 8.8 Hz, $4H_f$), 8.14 (d, J = 8.8 Hz, $4H_a$, $4H_b$ and $4H_c$), 7.45 (d, J = 8.8 Hz, $4H_e$), 7.34 (d, J = 8.8 Hz, $4H_d$). ^{13}C NMR (CD_2Cl_2:$MeSO_3H$ 5:1, 100 MHz), δ (ppm): 202.9, 167.6, 158.0, 147.7, 140.0, 136.8, 135.3, 130.9, 130.5, 128.7, 124.9, 121.8, 120.4, 119.0.

Polymer 6c (0.73 g, 99% Yield). T_g = 192 °C; η_{inh} = 0.75 dL g^{-1}. ^{1}H NMR (CD_2Cl_2:$MeSO_3H$ 5:1, 250 MHz), δ (ppm): 8.25 (d, J = 8.8 Hz, $4H_b$), 8.15 (br, $4H_c$ and $4H_a$), 7.60 (d, J = 7.9 Hz, $4H_f$), 7.33 (d, J = 7.9 Hz, $4H_d$ and $4H_e$). ^{13}C NMR (CD_2Cl_2:$MeSO_3H$ 5:1, 100 MHz), δ (ppm): 202.1, 169.2, 153.8, 147.6, 140.5, 135.2, 132.4, 130.7, 128.7, 125.4, 123.9, 122.6, 120.9, 118.5.

Polymer 7c (0.58 g, 96% Yield). T_g = 225 °C; η_{inh} = 0.76 dL g^{-1}. ^{1}H NMR (CD_2Cl_2:$MeSO_3H$ 5:1, 250 MHz), δ (ppm): 8.24 (d, J = 8.9 Hz, $4H_b$), 8.14 (br, $4H_a$ and $4H_c$), 7.88 (br, $2H_g$), 7.79 (d, J = 8.9 Hz, $2H_f$), 7.40 (d, J = 8.9 Hz, $2H_e$), 7.31 (d, J = 8.9 Hz, $4H_d$). ^{13}C NMR (CD_2Cl_2:$MeSO_3H$ 5;1, 100 MHz), δ (ppm): 201.6, 170.7, 154.6, 148.7, 147.4, 140.6, 135.1, 130.7, 128.6, 125.2, 123.4, 121.1, 118.1, 113.7, 110.4.

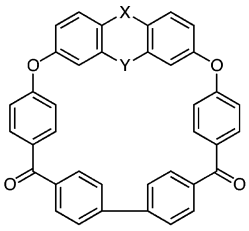
3. Results and Discussion

3.1. Determination of Macrocycle Strain-Enthalpies from Melt-Phase Polymerization. From the range of highly strained macrocycles described in the preceding paper,[1] the ether−ketones **1**−**4** (Chart 1) were selected for detailed investigation of their ring-opening polymerization chemistry. Initial DSC studies (10 °C min^{-1} heating rate, under nitrogen) showed that the sharp melting endotherms of these macrocycles (T_m = 354, 387, 353, and 410 °C for **1**−**4** respectively) were fully reproducible on succesive heating scans indicating that, despite their very evident ring-strain, such macrocycles are stable toward thermolytic ring-opening at temperatures exceeding 400 °C.

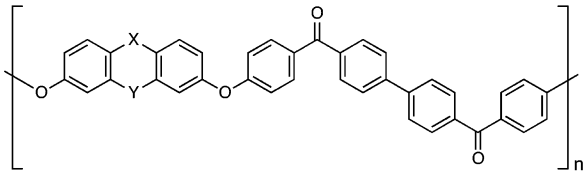
However, addition of a nucleophilic initiator such as cesium fluoride or potassium 4-benzoylphenoxide (1−5 wt % relative to macrocycle) led to very different results. For example, in the presence of 3 wt % of potassium 4-benzoylphenoxide, the onset of the melting endotherm of the dibenzofuran-based macrocycle **3** was interrupted by a very strong exotherm at only slightly higher temperature (Figure 1). A second DSC scan, after cooling immediately from 20 °C above the macrocycle melting point to room temperature, showed only a glass transition at a temperature (221 °C) corresponding to the T_g of a polymer homologous with the starting macrocycle,[10] and indeed, inspection of the sample after removal from the DSC crucible confirmed that a tough, transparent, polymeric product had been formed (**7a**, Scheme 1).

Deconvolution of the DSC curve, using the enthalpy of fusion previously determined for the pure macrocycle, gave an enthalpy of polymerization for macrocycle **3** of 81 kJ mol^{-1}. Since the latter arises from conversion of the highly strained macrocycle to its homologous but strain-free polymer, without any net change in the number or types of bond, the observed enthalpy of polymerization is, to a good approximation, equivalent to the strain enthalpy of the starting macrocycle. The

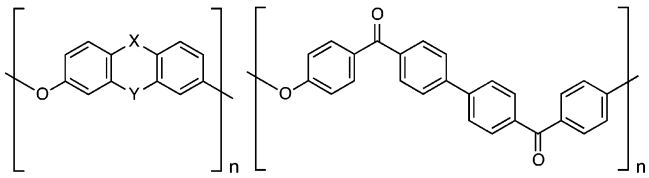
Chart 1. Highly Strained, Macrocyclic Aromatic Ether−Ketones and Their Homologous Polymers[a]



1 (X = SO_2, Y = H,H)
2 (X = $C(CF_3)_2$, Y = H,H)
3 (X = O, Y = direct bond)
4 (X = CO, Y = O)



5c (X = SO_2, Y = H,H)
6a, 6b, 6c (X = $C(CF_3)_2$, Y = H,H)
7a, 7b, 7c (X = O, Y = direct bond)



5a, 5b (X = SO_2, Y = H,H)
8a, 8b (X = CO, Y = O)

[a] Structures **5a**−**8b** represent random sequences of 2-ring and 4-ring units, in an overall 1:1 ratio, whereas **5c**−**7c** represent polymers with strictly alternating sequences of these units.

validity of this approach is confirmed by the absence of *any* detectable exotherm during the ring-opening polymerization of analogous but strain-free macrocycles (see for example ref 3n).

Attempts to polymerize the geometrically less-strained[1] macrocycles **1** and **2** in the melt, using the same level of potassium 4-benzoylphenoxide (3 wt %), gave incomplete reactions, but when the proportion of initiator was increased to 5 wt %, rapid, exothermic ring-opening polymerizations of these macrocycles were observed. The strain enthalpy released on polymerization of **3**, (81 kJ mol^{-1}) is markedly higher than that measured for **1** under the same conditions (54 kJ mol^{-1}), confirming that the presence of a fused ring system greatly increases the degree of ring-strain in otherwise similar macrocycles. Consistent with this, the dibenzofuran- and xanthone-based macrocycles **3** and **4** respectively both underwent rapid polymerization above their melting points in the presence of as little as 1 wt % of potassium 4-benzoylphenoxide initiator, though the polymerization exotherm of **4** extended to temperatures above 450 °C, where the onset of polymer decomposition might be anticipated. As a result the strain enthalpy of macrocycle **4** could not be quantified using this approach. However, with 3 wt % cesium fluoride as initiator, melting of **4** was followed immediately by polymerization, yielding a strain enthalpy of 86 kJ mol^{-1}, close to the value obtained for macrocycle **3**.

Values for the strain enthalpies of macrocycles **1**−**4** were determined using potassium 4-benzoylphenoxide ("KBZ") and/or cesium fluoride as initiators, across a range of initiator concentrations (1−10 wt %), and these values are shown in Table 1. The lack of any clear-cut dependence on initiator concentration, together with a generally good correlation between the strain enthalpies derived from analogous polymerizations using fluoride or aryloxide initiators strongly suggest that these ions are acting dynamically; i.e., they do not remain as end groups but are displaced from the growing chains as polymerization proceeds. As a result, the presence of the initiator makes little or no contribution to the overall enthalpy of polymerization.

Averaging the values shown in Table 1, the strain-enthalpies for macrocycles **1**, **2**, **3**, and **4** are estimated as 54 (± 2), 60 (± 3), 81 (± 4), and 87 (± 1) kJ mol^{-1} respectively. An order-of-magnitude figure for the strain energy of macrocycle **1** was also calculated by molecular mechanics (Cerius-2, Dreiding-II force field). Although the calculated value of ca. 70 kJ mol^{-1} is somewhat greater than that obtained experimentally for **1** (54 kJ mol^{-1}), it is completely consistent with the general range of strain enthalpies determined here for macrocycles of this type. To put these values of ring-strain in context, they may be compared to that of the highly strained molecule [2.2]-paracyclophane. In this molecule the ethanediyl bridges constrain the two benzene rings to an inter-ring distance (2.9−3.1 Å) less than the sum of their van der Waals radii (3.40 Å). As a result, the structure of [2.2]-paracyclophane is considerably distorted, with the aromatic rings displaying noticeably boatlike conformations.[11] The strain enthalpy calculated for [2.2]-paracyclophane is ca. 80 kJ mol^{-1},[12] a value very similar to the strain enthalpies of macrocyclic aromatic ether−ketones **3** and **4** determined here. However, in [2.2]paracyclophane, the strain is concentrated in only two heavily distorted aromatic rings, whereas the macrocycles studied in this work can distribute the strain by compressing bond angles at the ether, sulfone, and ketone linkages and by twisting and bending the biphenyl units.[1] There are no intramolecular $\pi-\pi$ repulsions to take account of, and so although small deviations from coplanarity are observed for the carbon atoms involved in the "biphenylene" aromatic rings, the aromatic residues in these macrocycles are otherwise essentially planar.[1]

3.2. Polymerization in Solution. The polymers obtained in this work by melt-phase ring-opening were at best only partially soluble in 98% sulfuric acid, due to a slight degree of cross-linking.[5] This disadvantage of melt-phase polymerization of macrocyclic aromatic ether−ketones in the presence of fluoride or phenoxide initiators was also noted by Hay et al., who investigated a number of different ionic initiators for the polymerization of macrocyclic aryl ethers.[9] In the melt phase, the order of activity for cations was found by these workers to be K > Na > Cs, but in solution, the order was Cs > Na. With potassium as cation, phenolate initiators followed the order of activity: 4,4′-biphenoxide > phenoxide > 4-phenoxyphenoxide > 4-phenylphenoxide, and overall, potassium 4,4′-biphenoxide proved the most effective initiator of all the salts investigated.[9]

Since melt-phase polymerization of strained macrocyclic ether−ketones gave only partially soluble polymers, the reactivity of of these macrocycles were next investigated in solution. Working initially with NMP as solvent and potassium 4,4′-biphenoxide ("KBP") as initiator, macrocycle **3** was found to undergo facile

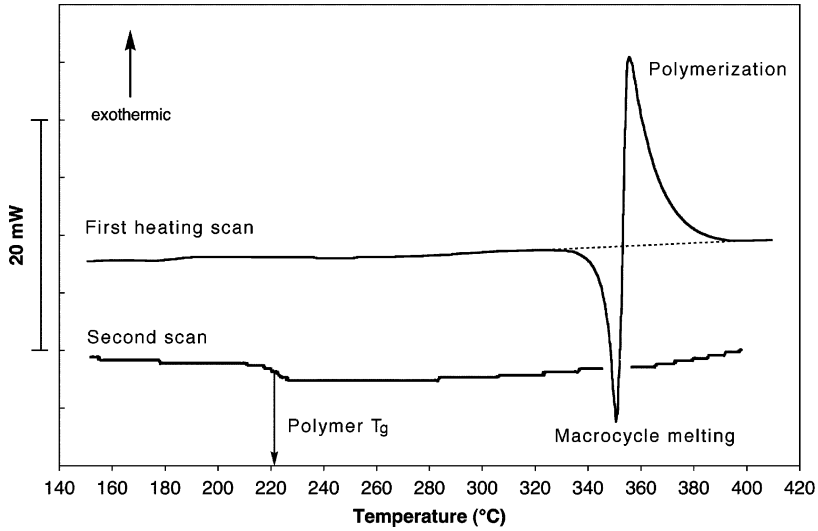
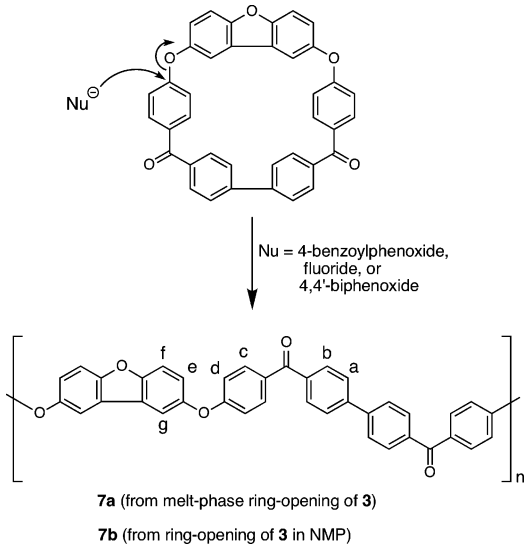


Figure 1. DSC thermograms showing polymerization of macrocycle **3** initiated by 3 wt % of potassium 4-benzoylphenoxide. The first heating scan shows the onset of melting of the macrocyle, followed by rapid, exothermic ring-opening polymerization; the second scan (lower trace) shows only the glass transition of the resulting poly(ether−ketone) **7a**.

Scheme 1. Nucleophilic Ring-Opening Polymerization of Macrocycle 3



7a (from melt-phase ring-opening of **3**)

7b (from ring-opening of **3** in NMP)

solution-phase polymerization at 200 °C. The polymerization was monitored by periodically quenching an aliquot of the reaction mixture in methanol and analyzing the precipitate by ^{1}H NMR. The progressive disappearance of two doublet resonances characteristic of the macrocycle, at δ 7.73 and 8.07, gave a quantitative measure of macrocycle conversion.

Working at 1 mol % of KBP initiator, both macrocycle conversion and polymer inherent viscosity (η_{inh}) increased rapidly with time (Table 2). After 30 min conversion reached 75% and η_{inh} was 0.43 dL g^{-1}, but after 2 h no further increase in conversion or inherent viscosity occurred, with these plateauing at values of 85% and 0.67 dL g^{-1} respectively. However, in the presence of 2 mol % of KBP, conversion rose very rapidly over the first 30 min and reached 100% (i.e., no residual macrocycle detectable by ^{1}H NMR) in less than 1 h. The inherent viscosity of the polymer leveled off at ca. 1.0 dL g^{-1} after 2 h.

The effects of macrocycle concentration on ring-opening polymerization were also investigated, with results showing that the conversion of macrocycle

Table 2. Ring-Opening Polymerization of Macrocycle 3 in Solution in NMP[a]

	1 mol % initiator (KBP)[b]		2 mol % initiator (KBP)[b]	
reaction time (min)	conversion (%)	η_{inh} (dL g^{-1})	conversion (%)	η_{inh} (dL g^{-1})
10	35	0.15	91	0.41
30	75	0.43	94	0.58
60	76	0.70	100	0.73
120	84	0.66	100	1.10
180	85	0.68	100	0.94
240	87	0.67	100	1.00

[a] Concentration: 0.5 mol L^{-1}; temperature: 200 °C. [b] KBP = potassium 4,4′-biphenoxide.

Table 3. Solution Ring-Opening Polymerization of Macrocycle 3 at Different Concentrations[a]

macrocycle concentration (M)	0.1	0.2	0.5	0.7
conversion of macrocycle (%)	94	98	95	99
final inherent viscosity (dL g^{-1})	0.05	0.47	0.97	1.07

[a] Polymerizations in NMP at 200 °C for 2 h in the presence of 2 mol % potassium 4,4′-biphenoxide.

increases only slightly with concentration, while the inherent viscosity of the polymer produced increases very substantially (Table 3). We have recently shown that, when carried out at high dilution, nucleophilic ring-opening of small macrocyclic aromatic ethers leads not to polymerization but instead to *ring-expanding homologation* (i.e., formation of higher macrocyclic oligomers),[6] and this type of reaction clearly accounts for the marked reduction in inherent viscosities observed here for polymerizations carried out at or below 0.2 M concentration of **3**.

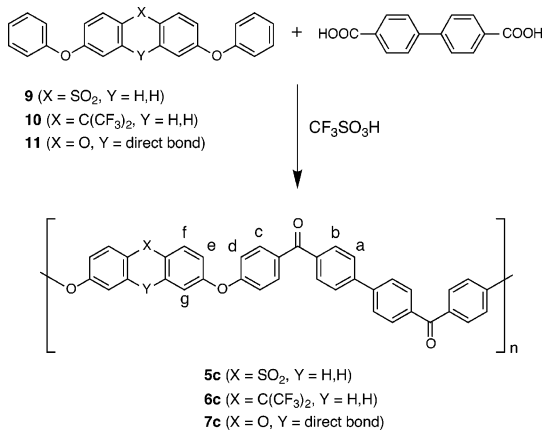
Despite the facile ring-opening polymerization of macrocycle **3** in NMP, attempts to achieve analogous polymerizations of macrocycles **1**, **2**, and **4** were not successful, either because the starting macrocycle showed only poor solubility in NMP at 200 °C (**1** and **4**) or because only low molar mass polymer (η_{inh} < 0.2 dL g-1) was obtained (macrocycle **2**). The high-boiling and chemically inert solvent diphenyl sulfone was therefore investigated as an alternative medium for polymerization of macrocycles **1**, **2**, and **4**. This solvent is used in the manufacture of aromatic poly(ether−ketone)s at temperatures of up to 320 °C,[13] and here it was used to explore ring-opening polymerizations at up to 250 °C.

Table 4. Ring-Opening Polymerization of Macrocycles 1, 2, and 4 in Diphenyl Sulfone Solution[a]

macrocycle	polymer	yield (%)	η_{inh} (dL g^{-1})	polymer T_g (°C) (midpoint)
1	**5b**	92	1.32	221
2	**6b**	90	1.15	188
4	**8b**	94	1.78	241

[a] Polymerizations carried out at 30 wt % macrocycle concentration in DPS at 250 °C for 2.5 h, in the presence of 2 mol % potassium 4,4′-biphenoxide.

Scheme 2. Syntheses of Reference Poly(ether−ketone)s with Regularly Alternating Monomer Sequences



At this temperature, all three macrocyclic monomers proved fully soluble, and polymerizations were found to proceed very rapidly, yielding high molar mass poly(ether−ketone)s (η_{inh} > 1.10 dL g^{-1}).

Results for polymerization of macrocycles **1**, **2**, and **4** are shown in Table 4. The polymers formed were of very high inherent viscosity, higher indeed than for any previously reported poly(ether−ketone) obtained by ring-opening polymerization. An outstanding characteristic of these polymers is that they are fully soluble in a range of solvents, including 98% sulfuric acid (used for viscometric measurements) and also in methanesulfonic acid/dichloromethane mixtures (used for NMR analyses). Although previously reported solution phase polymerizations involving *strain-free* macrocyclic ether−ketones also afforded soluble products, such reactions gave relatively low conversion of macrocycle and yielded only low molar mass polymers.[9]

3.3. Electrophilic Syntheses of "Reference" Polymers: To help determine the molecular structures of poly(ether−ketone)s formed by ring-opening polymerization in solution, a series of reference polymers with the same chemical composition were also prepared by electrophilic polycondensation of aromatic diethers **9**, **10**, and **11** with biphenyl-4,4′-dicarboxylic acid, using trifluoromethanesulfonic acid, CF_3SO_3H, as both solvent and catalyst (Scheme 2).[14]

A slight excess (2 mol %) of the diether was used to end-cap the polymer chain, in order both to control the final molecular weight and to stabilize the product. The results of these polymerizations are shown in Table 5. All three linear polymers were obtained in very high yield and proved amorphous, with good solubility in organic solvents. Their ^{1}H and ^{13}C NMR spectra showed that the polymerizations proceeded with excellent selectivity for all-para substitution.

3.4. Polymer Sequence Distribution as a Function of Macrocycle Structure. As the syntheses of polymers **5c**, **6c**, and **7c** represent electrophilic rather than nucleophilic substitutions, these polymers should have strictly alternating sequences of diether and diacid residues. This was confirmed by their ^{13}C NMR spectra which showed exactly the predicted numbers of resonances. Comparison of the spectrum for **6c** with that obtained for polymer **6b** obtained by nucleophilic ring-opening polymerization in DPS solution (Figure 2) clearly indicated that **6b** *also* contained an essentially alternating sequence of monomer residues. The same situation was observed for polymers **7c** and **7b** (obtained by electrophilic polycondensation and nucleophilic ring-opening in NMP respectively).

Table 5. Polycondensations of Aromatic Diethers with 4,4′-Biphenyldicarboxylic Acid[a]

diether monomer	polymer formed	yield (%)	η_{inh} (dL g^{-1})	T_g (°C) (midpoint)
9	**5c**	97	0.76	225
10	**6c**	99	0.75	188
11	**7c**	92	0.73	225

[a] In trifluoromethanesulfonic acid at 25 °C for 26 h, using a 56:1 mole ratio of CF_3SO_3H:diether and a 2 mol % excess of diether over dicarboxylic acid.

However, the spectrum of the ring-opened polymer **5b** (Figure 3) was far more complex than that of its counterpart **5c** obtained by electrophilic polycondensation. Numerous peaks observed for **5c**, including the carbonyl resonance, were split to give 1:1 doublets in the spectrum of **5b**, implying that this polymer comprises a *random* distribution of [−OArSO$_2$Ar−] (S) and [−OArCOArArCOAr−] (K) subunits and thus contains equal populations of carbonyl groups in the two different "monomer"- sequences [−OArCOArArC*OAr−OArCOArArCOAr−] and [−OArCOArArC*OAr−OArSO$_2$Ar−], where "Ar" = 1,4-phenylene and C* represents the carbonyl carbon atom being observed.

The random-sequence polymer **5b** has in fact been obtained previously by nucleophilic polycondensation of 4,4′-dihydroxydiphenyl sulfone with 4,4′-bis(4-fluorobenzoyl)biphenyl in the presence of potassium carbonate (Scheme 3).[10] Here, transformation from the originally expected alternating structure to a random one resulted from reversible cleavage of the ether linkages by fluoride and phenoxide nucleophiles during polymerization. Such cleavage reactions, being activated by electron withdrawing groups on *both* adjacent aromatic rings, lead to an essentially random sequence of "K" and "S" residues.[10] Further details of the assignments of ^{13}C NMR resonances for this particular polymer are given in ref 10.

Macrocycle **1** is clearly susceptible to nucleophilic ring-opening at two alternative positions, para to sulfone and para to ketone (Scheme 4), so that formation of a nonalternating structure for polymer **5b** is readily accounted for. Formation of the *fully* random chain-sequence implied by its ^{13}C NMR spectrum is less easily explained, since sulfone is a more strongly activating substituent than ketone and nucleophilic attack on the sulfone-bearing ring should therefore be favored. However, in this particular macrocycle, sulfone also acts as a strongly stabilizing substituent for the aryloxide leaving group resulting from attack on the *ketone*-bearing ring, so enhancing the rate of macrocycle cleavage at this position and—evidently—equalizing the probability of ring-opening at the two alternative sites. As noted above, nucleophile-promoted ether exchange *after* ring-opening can also provide a possible route to

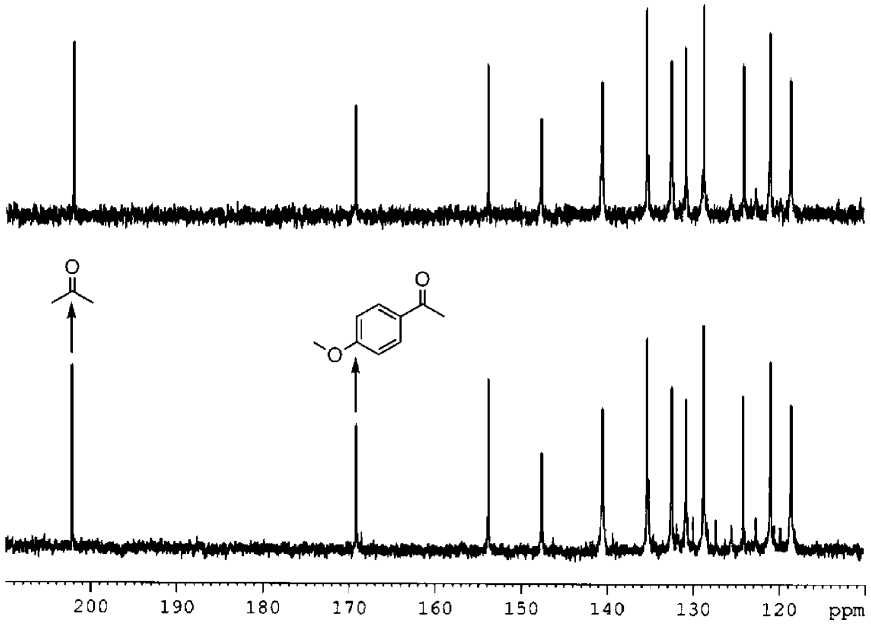


Figure 2. ^{13}C NMR spectra of the alternating-sequence reference polymer **6c** (above), produced by electrophilic polyacylation in trifluoromethanesulfonic acid (Scheme 2), and polymer **6b** (below) obtained by nucleophilic ring-opening polymerization of macrocycle **3** in DPS solution. Minor resonances in the spectrum of **6b** are assigned to traces of residual macrocycle, but the spectra of the two polymers are otherwise essentially identical.

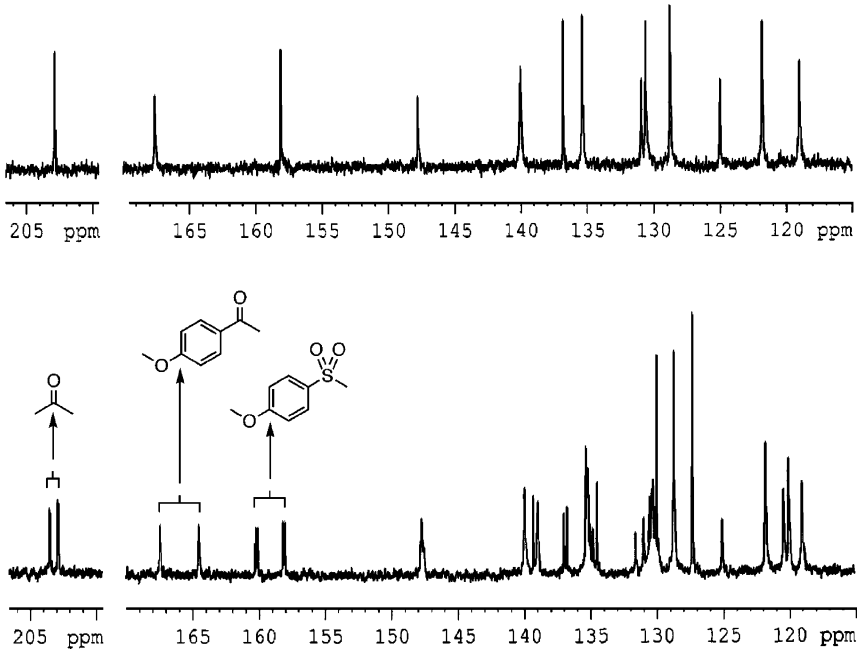


Figure 3. ^{13}C NMR spectra of the alternating-sequence reference polymer **5c** (above), produced by electrophilic polyacylation in trifluoromethanesulfonic acid (Scheme 2), and polymer **5b** (below) obtained by nucleophilic ring-opening polymerization of macrocycle **3** in DPS solution (Scheme 4).

sequence randomization,[10] and indeed both mechanisms (two-site attack and subsequent ether exchange) could well be operative in this type of ring-opening polymerization.

As with macrocycle **1**, the ether-linkages of macrocycle **4** are activated by different electron-withdrawing para-substituents on adjacent rings, specifically (i) a carbonyl group within the xanthone unit and (ii) a simple ketone linkage. During ring-opening polymerization, the initiator can attack either adjacent ring (Scheme 5), again leading to an irregular sequence, in this case of [−O−xanthone−] (X) and [−OArCOArArCOAr−] (K) subunits (polymer **8b**). The ^{13}C NMR spectrum of the product (Figure 4) indeed confirmed that polymer **8b** contains approximately equal populations of carbonyl groups (resonances at ca. 202 ppm) associated with the doublet sequences "KX" and "KK".

The size of the "K" subunit (four aromatic rings) means that the ketonic carbonyl groups are very much closer to one neighboring residue than the other, and so ^{13}C NMR can only distinguish *doublet* sequences using this resonance. However, the carbonyl carbon of the much smaller xanthone unit should be sensitive to the nature of *both* adjacent residues, and so could in principle provide information on the proportions of the various *triplet* sequences present in the copolymer. For a truly random-sequence polymer, the xanthone-centered triplet sequences (XXX, XXK, KXX, and KXK)

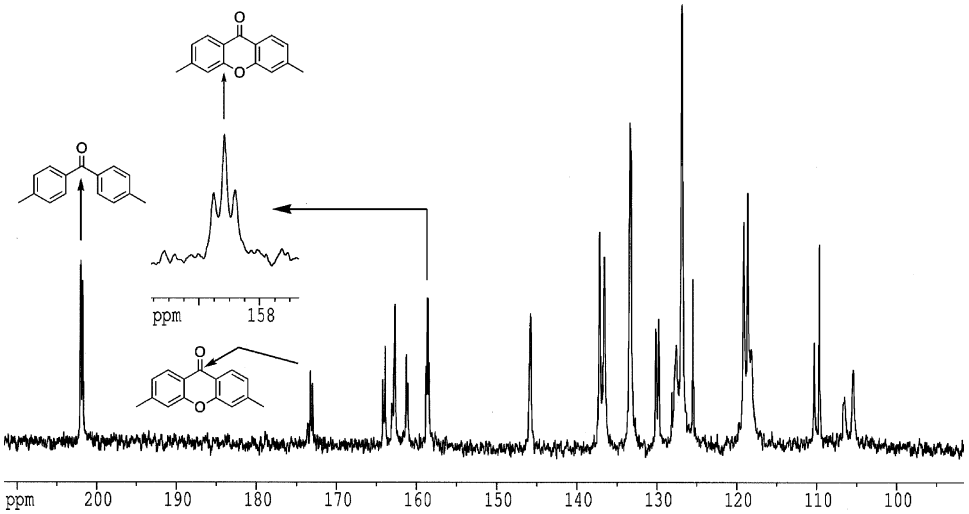
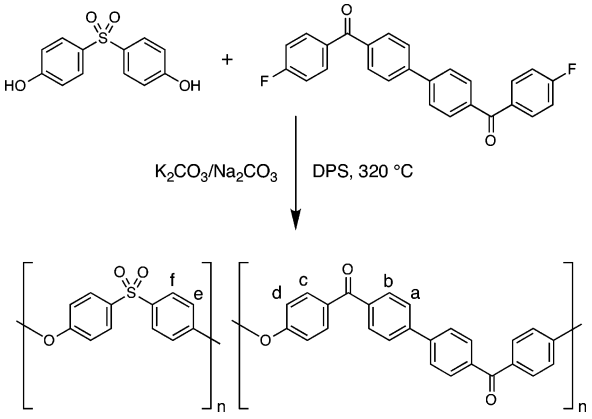
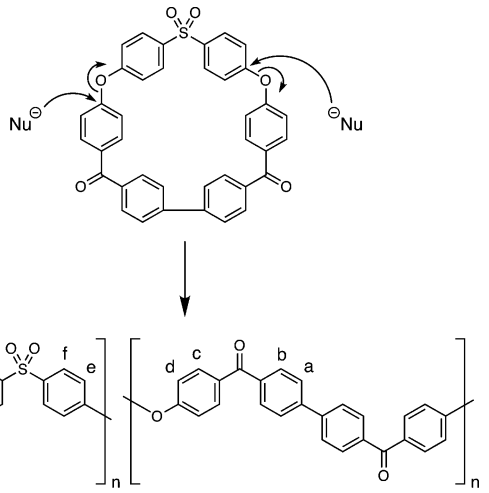


Figure 4. ^{13}C NMR spectrum of polymer **8b**, obtained by nucleophilic ring-opening polymerization of macrocycle **4** in diphenyl sulfone solution (Scheme 5).

Scheme 3. Synthesis of a Random-Sequence Polymer Equivalent to the Ring-Opened 5b via Nucleophilic Polycondensation and Simultaneous Transetherification[10]

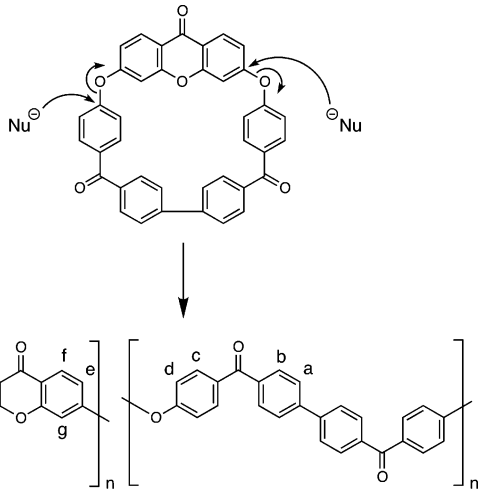


Scheme 4. Formation of the Random-Sequence Polymer 5b via Nucleophilic Ring-Opening at Two Alternative Ring Positions of Macrocycle 1



5a (from melt-phase polymerization)
5b (from solution-phase polymerization in DPS)

Scheme 5. Formation of the Irregular-Sequence Polymer 8b via Nucleophilic Ring-opening at the Two Alternative Ring-positions of Macrocycle 4



8a (from melt-phase polymerization)
8b (from solution-phase polymerization in DPS)

should occur in the ratio 1:1:1:1, and since the central xanthone-carbonyl groups in the sequences XXK and KXX are chemically equivalent, this carbon should give rise to three resonances of relative intensity 1:2:1. Three resonances are indeed observed for the xanthone carbonyl group in polymer **8b**, at ca. 173 ppm (Figure 4), although their intensities are closer to 1:4:3 than 1:2:1, apparently indicating that the sequence distribution is less than fully random. The intensities of carbonyl resonances are however notoriously sensitive to relaxation effects, and indeed a second xanthone resonance at ca. 158.5 ppm, assigned to the carbon ipso to heterocyclic oxygen, *does* shows an apparent 1:2:1 "triplet" (Figure 4, expansion). The unsymmetrical position of this carbon atom relative to neighboring X or K residues means that, as far as it is concerned, the sequences XXK and KXX are no longer equivalent and the observed pattern must comprise four *equal* resonances (seemingly now implying a fully random sequence distribution) with the central two being coincident. Further work is clearly required to determine whether the sequence distribution is fully random or not, but for the present it is clear that the multiplicity of resonances in the ^{13}C NMR spectrum of this polymer indicate a very substantial degree of sequence irregular-

ity, confirming that nucleophilic ring-opening of macrocycle **4** can occur at both types of aromatic ring adjacent to the ether linkages (Scheme 5).

4. Conclusions

Highly strained macrocyclic ether−ketones undergo ring-opening polymerization via ether exchange in the presence of nucleophilic initiators such as fluoride or phenoxide anions which reversibly cleave the ether linkages. Strain enthapies of these macrocycles, from DSC analyses of their exothermic ring-opening polymerization are in the range 50−90 kJ mol^{-1}. Melt-phase polymerization generally affords slightly cross-linked materials, but solution-phase polymerization at high macrocycle concentrations gives fully soluble, high molar mass polymers. Sequence analysis of the resulting polymers by ^{13}C NMR shows that alternating or random monomer sequences may be obtained, depending on whether one or both aromatic rings adjacent to the ether linkages are activated toward nucleophilic attack.

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