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Rapid, Uncatalyzed Ring-Opening Polymerization of Individual Macrocyclic Poly(arylene thioether ketone)s under Dynamic Heating Conditions

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ABSTRACT: Uncatalyzed, ring-opening polymerization of individual macrocyclic poly(arylene thioether ketone)s (**1**–**4**) and mixtures (**5**) under dynamic heating conditions has been demonstrated for the first time. High-molecular-weight, film-forming products were obtained after heating of the macrocycles up to 480 °C, with a heating rate of 10–20 °C /min. Depending on the macrocyclic structure and heat treatment conditions, the polymers obtained were amorphous or semicrystalline, soluble or slightly cross-linked. NMR analyses of the soluble polymers revealed their linear, highly regular structure. According to NMR, DSC, and TGA studies, the polymers obtained do not contain any residual macrocycles. The polymers with thio-*p*-arylene moieties in the main chain were thermally stable. The catalyzed ring-opening polymerization of **5** carried out in diphenyl sulfone solution is also reported for comparison. Using quantum mechanical calculations of the ring opening of macrocycles, a reaction mechanism is suggested. Preparation of nanosized poly(thioether ketone) fibrils by a replication method is described.

1. Introduction

Ring-opening polymerization (ROP) is a well-established method in polymer chemistry and plays an important role in the production of polymeric materials.[1–4] The method has been an active subject of academic and industrial research and many polymers, such as poly(dimethylsiloxane), poly(ethylene oxide), poly(butylene oxide), poly(iminoethylene), and nylon-6 were commercialized using this technique. Various macrocycles also became popular starting materials for the building of supramolecular assemblies, which thereby stimulated an additional interest within the field.[5–7] Recent discoveries of the ROPs of macrocyclic aromatic ether ketones[8–17] and macrocyclic oligomeric polycarbonates[4,18–20] have received a great deal of attention over the past decade.

An important advantage of macrocycle-based technology is that starting materials can be polymerized without generation of byproducts, and the products can be processed at much lower temperatures than the corresponding high-molecular-weight polymers because of their low melt viscosities. This allows the use of reactive processing techniques to transform cyclic monomers directly into commercial objects by use of such technologies as reaction–injection molding and melt pultrusion, which are of great importance in the production of high-performance materials of aromatic poly(arylene ether ketone)s.

From the very beginning, ROPs of pure arylene ether and arylene ether ketone macrocycles were carried out by the use of either potassium or cesium fluoride salts or alkali phenoxides and alkali benzoates. It is believed that ROPs of these compounds are initiated by nucleophilic attack of the fluoride ion or phenoxy anion on the carbon of aromatic nuclei and proceed as a transetherification reaction driven by the entropy change, since the macrocycles have little or no ring strain. Use of the initiators described may result in polymers containing inorganic salts and alkali-metal phenoxides as end groups, which may lead to thermooxidative instability of the polymers at elevated temperatures.

Another problem is generally incomplete conversion of the monomer (macrocycle), which results from uneven distribution of the catalysts and/or high viscosity or heterogeneity of the reaction medium. Because of these problems, the development of uncatalyzed ROP of macrocyclic precursors of the high performance polymers could be of great significance. In an effort to address the problems associated with ROP of macrocyclic homologues of high-performance polymers, facile,

free-radical ROPs of cyclic arylene thioethers, arylene ether thioethers, arylene ether thioether ketones, and arylene disulfides have been developed recently by the group of A. S. Hay.[21−31]

Macrocyclic arylene ether thioethers and arylene ether thioether ketones, in which sulfur atoms alternate with oxygen atoms in the backbone,
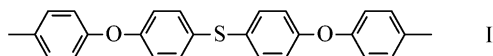

were mostly used for the studies. The ROP is achieved via a transthioetherification reaction involving thiyl radical(s) and can be promoted by use of a catalytic amount of elemental sulfur or disulfide organic compounds such as 2,2′-dithiobis(benzothiazole). The polymerizations performed in both the melt and in solution (generally, at 300−350 °C) are assumed to be initiated by the in situ generated thiyl radicals and proceed via a free-radical mechanism. The free-radical nature of the polymerizations promoted by elemental sulfur, diphenyl disulfide, or 2,2′-dithiobis(benzothiazole) was indicated by electron paramagnetic resonance (EPR) spectroscopy.[21,23] To the best of our knowledge, all of these ROPs were performed under isothermal conditions, in the temperature range 300−400 °C, mainly at 360−380 °C, with mixtures of macrocyclic oligomers.

It has also been demonstrated that free radical polymerizations of cyclic (arylene) disulfide oligomers[24,29,30] and the cyclic hexamer of phenylene sulfide or a mixture of cyclic phenylene sulfides[32,33] can be carried out free of catalyst, at temperatures generally below 170 and 320−350 °C, respectively.

The aim of the present work is to study uncatalyzed, nonisothermal ROPs of the individual macrocyclic arylene thioether ketones **1**−**4** containing, with phenylene spacer units, sulfur atoms alternating with carbonyl groups:
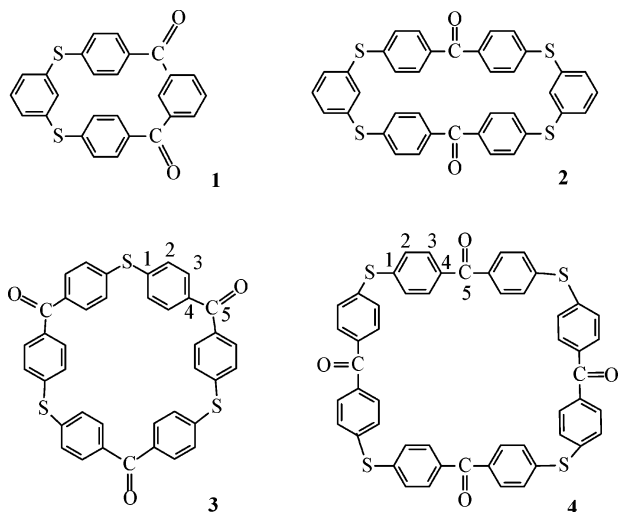
For comparison, macrocycle **6** with one sulfur atom in the ring was also used.
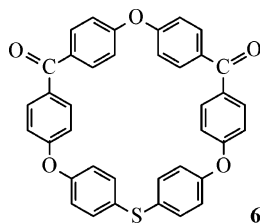
Macrocycles **1**−**4** and **6** were obtained by both high dilution and pseudo-high-dilution aromatic nucleophilic substitution reactions. Characterization of trimer **3**, previously characterized by only X-ray structural analysis, was completed with MALDI, NMR, and DSC studies. Macrocycles **1**, **4**, and **6** were obtained and characterized for the first time. A mixture, **5**, containing macrocycles **3** and **4**, was also used for studies.

Solution-catalyzed isothermal ROP of the macrocyclic mixture, **5**, was carried out in diphenyl sulfone for comparison. Structure and properties of the products obtained, and the reaction mechanism proposed, are described. An example of microfabrication of poly thioether ketones as nanosized fibrils is given.

2. Experimental Section

2.1. Materials. *N*-Methylpyrrolidinone (NMP, 99%), *N,N*-dimethylacetamide (DMAc, 99%), 1,3-benzenedithiol (99%), sodium sulfide (98%), 4,4′-dichlorobenzophenone (99%), and diphenyl sulfone (99%) were purchased from Aldrich. Macrocycle **2** was prepared according to the literature[34] and was purified additionally by recrystallization from NMP.

2.2. Measurements. Inherent viscosities of 0.2% polymer solutions in concentrated sulfuric acid were measured at 25 °C using a Schott-Gerate CT semiautomated viscometer. Proton and ^{13}C NMR spectra were recorded using Bruker DPX-300 and 250 MHz spectrometers. Polymers were dissolved in a $CH_3SO_3H/CDCl_3/CF_3SO_3H$ mixture to give 1% (w/v) solutions for NMR analysis. Melting points and glass transition temperatures (onset values) were determined by DSC under a nitrogen atmosphere, using a Mettler DSC 20 system calibrated with an indium/tin/zinc reference sample. Thermal stabilities and char yields were determined by thermogravimetric analysis (TGA) on a Perkin-Elmer Series 7 instrument. A heating rate of 10 °C/min in a nitrogen atmosphere was used to analyze samples. Infrared spectra (KBr pellets and films) were recorded on a Bruker Equinox 55 spectrometer with Bruker IRscope-II microscope attachment. X-ray crystal structures were determined using a Siemens P4/PC diffractometer with graphite-monochromated Cu Kα radiation and a Mar Research image plate system with Mo Kα radiation. Mass spectra (CI) were obtained on a VG Autospec instrument. Matrix-assisted laser desorption/ionization time-of-flight (MALDI−TOF) mass spectra were recorded on a Micromass TofSpec instrument instrument with a a wavelength of 337 nm (N₂ laser light, 3 ns pulse width, 100 μm diameter spot). The MALDI instrument was operated in a positive reflection mode. The ions produced from each laser shot were accelerated to 20 keV into a 1 m drift region. The sample was prepared by dissolving the oligomers in a CHCl₃/TFA/ mixture at a concentration of 5.0 mg/mL. The matrix used for the experiment was 1,8,9-anthracenetriol (dithranol) (Aldrich). Sodium trifluoroacetate (Aldrich) was used as the cationization agent with a stock solution containing 5.0 mg/ mL in tetrahydrofuran. A 10 μL portion of the sample solution and 10 μL of the sodium trifluoroacetate solution were added to 100 μL of a 10 mg/mL solution of the matrix dissolved in tetrahydrofuran. This final solution was shaken briefly, and 0.5 μL was applied to a stainless steel sample slide and air-dried prior to analysis.

2.3. Synthesis of Macrocyclic Monomers. Macrocycle **1** was obtained by cyclocondensation of 1,3-benzenedithiol with 1,3-bis(4-fluorobenzoyl)benzene. A solution of 1,3-benzenedithiol (1.00 g, 6.90 mmol) in DMAc (75 mL) and a solution of 1,3-bis(4-fluorobenzoyl)benzene (2.20 g, 6.80 mmol) in DMAc (75 mL) were added simultaneously, dropwise, under nitrogen to a refluxing suspension of potassium carbonate in DMAc (150 mL) and benzene (50 mL) over 6 h, with continuous (Dean−Stark) removal of water as a benzene azeotrope. The benzene was then removed by distillation and the reaction continued for a further 12 h at 130 °C. The mixture was cooled and poured into methanol/water (1:1, v/v, 500 mL), and the white precipitate was filtered off, washed with water and methanol,
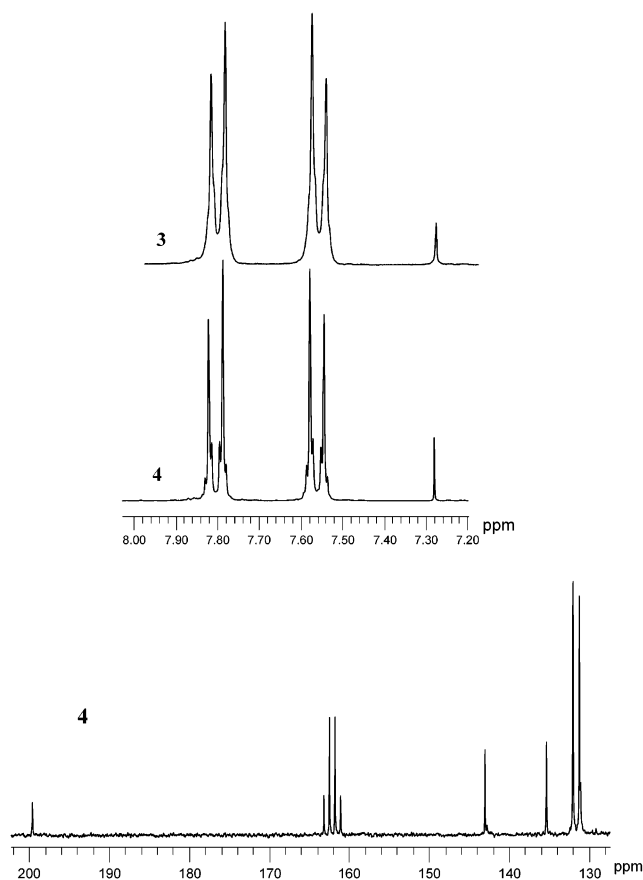
Figure 1. ^{1}H NMR (top) and ^{13}C NMR (bottom) spectra of macrocycles **3** and **4**. The singlet at 7.27 ppm in ^{1}H NMR and quartet at 162 ppm in ^{13}C NMR spectra are due to solvents (chloroform and trifluoroacetic acid, respectively).

Figure 2. X-ray crystal structures of macrocycles **1** (upper), **4** (center) and **6** (lower).

and dried. Column chromatography with dichloromethane/toluene (9:1, v/v) afforded macrocycle 1 (2.19 g, 75% yield).

Characterization Data for 1. Mp: 253 °C (DSC). ^{1}H NMR (CDCl$_3$, 250 MHz; δ, ppm): 8.29 (dd, 2H), 7.76 (tr, 1H), 7.53 (m, 6H), 7.46 (m, 2H), 7.40 (tr, 1H), 7.29 (d, 4H). ^{13}C NMR (CDCl$_3$, 75 MHz) (δ, ppm): 195.1, 143.6, 137.0, 136.7, 136.5, 136.3, 135.8, 132.6, 130.8. 130.7, 130.4, 129.7. MS (CI): m/z = 425 [M + H]$^+$. Anal. Calcd: C, 73.60; H, 3.80; S, 15.10. Found: C, 73.20; H, 3.85; S, 15.50. Single crystals suitable for X-ray analysis (Figure 2) were grown by vapor diffusion of a solution in dichloromethane with hexane.

Crystal Data for 1. C$_{26}$H$_{16}$O$_2$S$_2$, M = 424.51, orthorhombic, space group $P2_12_12_1$, a = 9.2464(8), b = 10.2802(8), and c = 21.814(4) Å, V = 2073.5(4) Å^3, T = 293 K, Z = 4, D_c = 1.360 g cm^{-1}, μ(Cu Kα) = 2.5 mm^{-1}, F(000) = 880. From a total of 1792 independent measured reflections, agreement factors R_1 = 0.0673 and wR_2 = 0.1750 were obtained for 1239 independent observed reflections [$I > 2\sigma(I)$].

Macrocycle **2** was prepared according to method[34] and purified additionally by recrystallization from NMP.

Macrocycle **3** was synthesized as described by Ovchinnikov et al.,[35] with slight modifications. A mixture of sodium sulfide (7.41 g, 95.50 mmol) and 4,4′-dichlorobenzophenone (23.84 g, 95.0 mmol) in 1.0 L of NMP was stirred under nitrogen flow at 200 °C for 14 h. The reaction mixture was cooled and poured into 2.0 L of water. The suspension formed was acidified with HCl to pH ~ 5 and stirred overnight. After filtration, washing with water, and drying, the cream-colored powder was extracted with dichloromethane for 12 h. Evaporation of the extract afforded 5.20 g of dark gray powder. After two recrystallizations from chlorobenzene, a mixture of macrocycles **3** and **4** (2.80 g) in 3:2 mole ratio was obtained (**5**). Chromatography of 0.60 g of the mixture with dichloromethane on silica gel allowed the trimer **3** (0.22 g) and the tetramer **4** (0.18 g) to be isolated as pure compounds. Their identities were
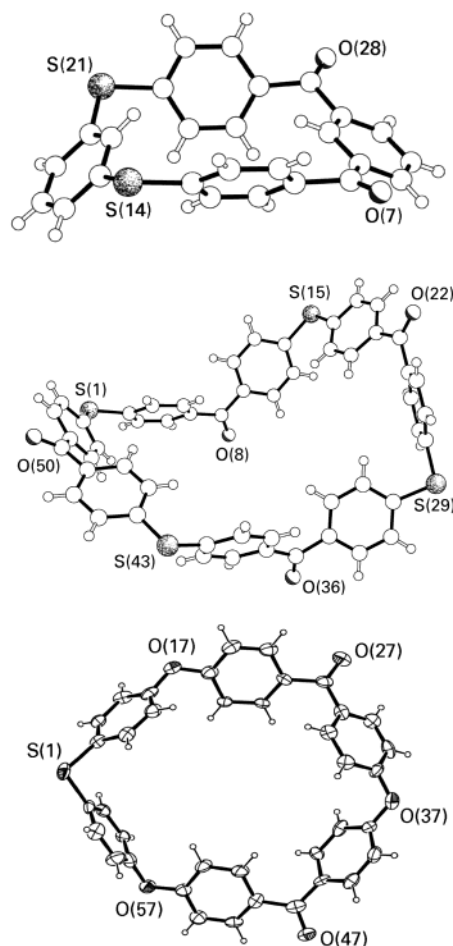
confirmed by DSC, MALDI−TOF MS analysis, and NMR spectroscopy (Figure 1).

Characterization Data for 3. Mp: 450 °C (DSC). ^{1}H NMR (CDCl$_3$/TFA, 250 MHz; δ, ppm; J_{HH}, Hz): 7.80 d (J = 8.54, 12H, H^3), 7.56 d (J = 8.54, 12H, H^2). ^{13}C NMR (CDCl$_3$/CH$_3$-SO$_3$H/CF$_3$SO$_3$H, 62.5 MHz; δ, ppm): 200.59 (C^5), 142.83 (C^1), 135.41 (C^4), 131.74 (C^2), 130.51 (C^3). MS (MALDI−TOF, dithranol matrix, CF$_3$COONa cationizing agent): m/z = 659 [M + Na]$^+$.

Characterization Data for 4. Mp: 439 °C (DSC). IR (KBr): 1655 cm^{-1} (ν(C=O)). ^{1}H NMR (CDCl$_3$/TFA, 250 MHz; δ, ppm; J_{HH}, Hz): 7.80 d (J = 8.64, 16H, H^3), 7.56 d (J = 8.64, 16H, H^2). ^{13}C NMR (δ, ppm): 199.58 (C^5), 142.98 (C^1), 135.29 (C^4), 131.99 (C^2), 131.18 (C^3). MS (MALDI−TOF, dithranol matrix, CF$_3$COONa cationizing agent): m/z = 871 [M + Na]$^+$. Single crystals suitable for X-ray (Figure 2) analysis were grown by vapor diffusion of a solution in dichloromethane/trifluoroacetic acid with diethyl ether.

Crystal Data for 4. C$_{52}$H$_{32}$O$_4$S$_4$, M = 849.02, monoclinic, space group $P2_1/c$, a = 13.773(2), b = 31.364(3), and c = 34.626-(5) Å, β = 96.26(1)°, V = 14 869(3) Å^3, T = 293 K, Z = 12 (3 independent molecules), D_c = 1.138 g cm^{-1}, μ(Cu Kα) = 2.08 mm^{-1}, F(000) = 5280, 20 403 independent measured reflections, R_1 = 0.088, wR_2 = 0.232 for 10 978 independent observed reflections [$I > 2\sigma(I)$].

The novel macrocycle **6** was obtained and characterized as follows. A solution of 4,4′-bis(4″-fluorobenzoyl)diphenyl ether (4.14 g, 10.00 mmol) and 4,4′-thiodiphenol (2.18 g, 10.00 mmol) in N,N-dimethylacetamide (DMAc, 100 mL) was added under nitrogen via a syringe pump (injection rate 2 mL h^{-1}) to a stirred refluxing suspension of potassium carbonate (2.07 g, 15.00 mmol) in DMAc (400 mL) and toluene (200 mL). 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 acidified water (1 L) giving a cream precipitate which was filtered off, washed with water and methanol, dried, and extracted with dichloromethane for 12 h. Fractionation of the extract by column chromatography (dichloromethane eluent) afforded macrocycle **6** (0.88 g, 15% yield).

Characterization Data for 6. Mp: 439 °C (DSC). ^{1}H NMR (CDCl$_3$/TFA, 250 MHz; δ, ppm; J_{HH}, Hz): 7.72 (d, $J = 8.9$, 4H), 7.71 (d, $J = 8.8$, 4H), 7.53 (d, $J = 8.7$, 4H), 7.10 (d, $J = 8.7$, 4H), 7.07 (d, $J = 8.8$, 4H), 7.03 (d, $J = 8.9$, 4H). ^{13}C NMR (CDCl$_3$/TFA, 62.5 MHz; δ, ppm): 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. MS (CI): $m/z = 592.13$ [M]$^+$; calcd for C$_{38}$H$_{24}$O$_5$S, 592.14. Anal. Calcd: C, 77.02; H, 4.05. Found: C, 77.03; H, 4.02. Single crystals suitable for X-ray analysis (Figure 2) were grown by vapor diffusion of a solution in dichloromethane/trifluoroacetic acid with diethyl ether.

2.4. Polymer Syntheses. Ring-opening polymerizations under dynamic heating conditions were carried out by means of a Mettler DSC 20 system. Macrocycle samples (5−6 mg) were placed in DSC aluminum pans and measurements were made from 60 to 360−480 °C at a scanning rate of 10−20 °C/min under nitrogen. Second and third scans were performed on some samples by heating to the desired temperature and quench cooling to room temperature before analysis.

Catalyzed ring-opening polymerization of the mixture **5** was performed by high-temperature solution polycondensation. The reaction was conducted in a 5 mL tube equipped with a nitrogen inlet and mechanical stirrer. The reaction vessel was charged with **5** (0.225 g), diphenyl sulfone (0.600 g, 2.75 mmol), and the potassium salt of 9,9-bis(4-hydroxyphenyl)fluorene (0.006 g, 0.016 mmol). The resulting mixture was heated to 310 °C, whereupon a clear solution was obtained. In 2 h a viscous solution formed was poured into methanol. The resulting suspension was washed thoroughly with methanol, water, and acetone. The yield of polymer **5b** was 0.215 g (95.5%).

2.5. Molecular Modeling. Calculations were performed with Jaguar 4.2 suite of programs. Global minimum structures were located using the Monte Carlo conformational search method implemented in Macromodel 8.0 suite of programs for all cyclic and open-chain molecules using the MMFF force field. Located minimum energy conformers were used as input geometries for Jaguar 4.2. Geometry optimizations were run with B3LYP hybrid functional[36−39] using standard 6-31G* basis set with no symmetry restrictions. Closed-shell and open-shell systems were treated using restricted and unrestricted formalism, respectively. Frequency jobs were run for all structures except for macrocycle **4** to calculate entropy, enthalpy, and free Gibbs energy as well as to ensure that minimized structures had been located (zero imaginary frequencies). Because of the size of macrocycle **4** only total electronic energies are available, which correspond approximately to the enthalpy.

3. Results and Discussion

3.1. Synthesis of Macrocycles. Syntheses of individual, single-sized macrocycles were performed using high- and pseudo-high-dilution conditions, under which intramolecular cyclization is favored relative to intermolecular linear step-growth polymerization. This is a well-established method for the macrocyclic preparations.[40] The presence of trace amounts of potassium salts can lower the melt stability of cyclic arylene ether sulfone oligomers.[9,23] Therefore, to avoid the undesirable process of premature polymerization, potassium-containing materials were not used in the course of macrocycle preparation and purification.

The polycondensation of equimolar amounts of 4,4′-dichlorobenzophenone with sodium sulfide followed by methylene chloride extraction of the low-molecular-weight polymer obtained afforded a mixture of oligo-
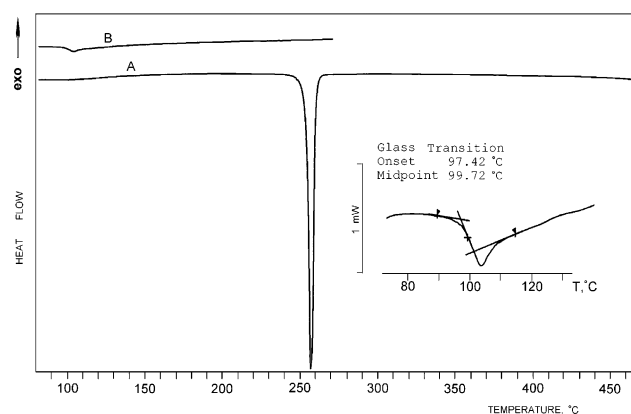
Figure 3. DSC thermograms of macrocycle **1**: (A) first heating scan; (B) second heating scan.

mers. MALDI TOF MS analysis of the mixture revealed the presence of cyclic products up to the cyclic hexamer ($2 \leq n \leq 6$). Recrystallization of the extract from chlorobenzene gave a mixture of macrocycles **3** and **4**, approximately in a 3:2 ratio. After separation of the mixture by column chromatography individual compounds (according to TLC and MALDI data) **3** and **4** were obtained. The melting behavior of the products will be discussed below.

Well-resolved NMR spectra and X-ray structures of the compounds, presented in Figures 1 and 2, unambiguously confirm their cyclic structures. The ^{1}H NMR spectra of **3** and **4** are very similar, and their ^{13}C spectra are also virtually identical.

In addition to individual compounds, we also used a mixture, **5**, of macrocyles **3** and **4**, obtained by recrystallization from chlorobenzene (see Experimental Section) and additionally purified by recrystallization from chlorobenzene with charcoal**.** It is to be noted that use of macrocyclic mixtures is widespread in macrocycle-based polymer chemistry. Apart from the obvious advantages of eliminating the separation step, macrocycle mixtures very often possess lower melting points, which is important for melt ring-opening polymerizations.

Interestingly, the mixing of **3** with **4** lowers the melting peak of the tetramer only, which appears at 408 °C (instead of 439 °C for the pure compound), whereas trimer **3** melts at the same temperature (449 °C).

3.2. Ring-Opening Polymerization of the Macrocycles. 3.2.1. Ring-Opening Polymerizations under Dynamic Heating Conditions. DSC analysis of **1** performed at a heating rate of 20 °C/min (Figure 3A) reveals sharp melting at 257 °C and no other heat transitions up to 480 °C. The second DSC scan (Figure 3B) showed a well-resolved glass transition at 99 °C. In principle, many aromatic poly(ether ketone)s and polythioether macrocycles possess glass transitions, but more significantly, after the first scan the sample, depending on the amount in the DSC pan, appears to be either a homogeneous, transparent, light green-brown tough material or a thin, flexible, elastic film.

Therefore, the heating of sample **1** under dynamic heating conditions affords polymeric material (**1a**), which appears to be slightly cross-linked, judging from its insolubility and appreciable swelling behavior in concentrated sulfuric acid.

The first DSC scan of macrocycle **2**, performed under similar conditions used for treatment of **1**, showed a melting peak at 327 °C. A fine crystalline powder of **2** also transforms into tough, elastic material after the
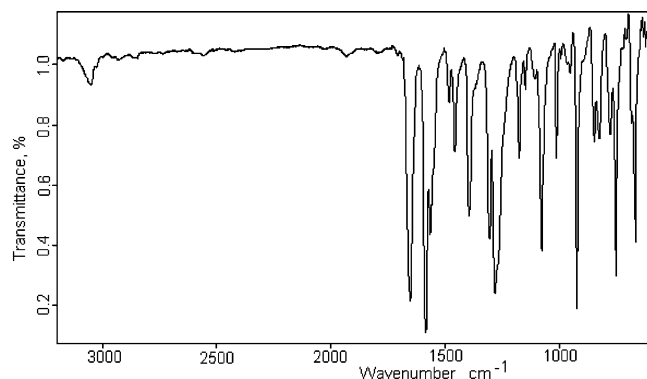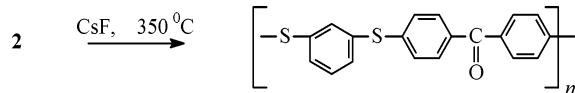
Figure 4. IR spectrum of polymer **2a** (film).
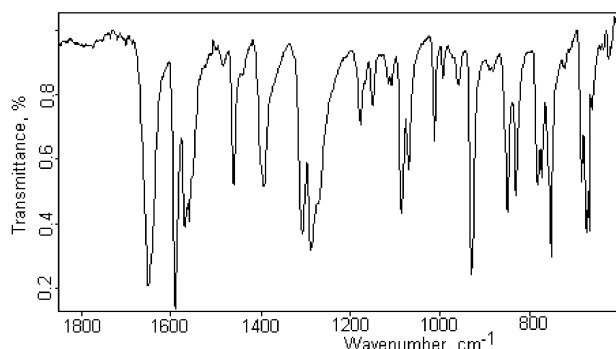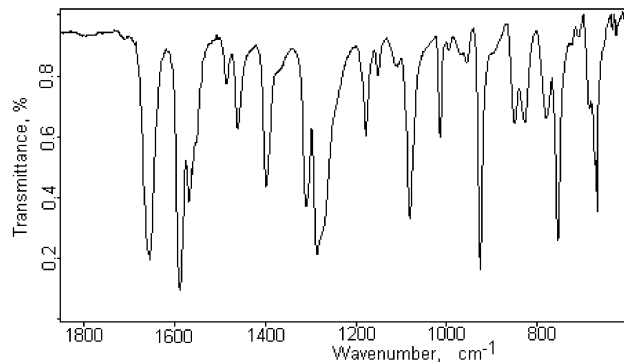
Figure 5. IR spectra of polymer **2a** film (top) and macrocycle **2** (bottom), tablet with KBr.

first scan, and glass transition at 109 °C was observed during the second scan. The T_g observed coincides perfectly with the T_g of the polymer obtained previously by anionic ROP of **2** in the presence of 4-hydroxybenzophenone.[34]

Therefore, dynamic heating of samples **1** and **2** affords slightly cross-linked polymeric material, as judged from insolubility and swelling of the samples in concentrated sulfuric acid.

The IR spectrum of **2a** after the first scan up to 480 °C (Figure 4) shows a clean, well-resolved set of signals. Expansion of the fingerprint region of the spectra (Figure 5) reveals the expected presence of the band at 1655 cm^{-1}, corresponding to stretching vibrations of the carbonyl group, intense bands at 1587, 1458, and 1396 cm^{-1}, originated by skeletal vibrations of aromatic nuclei, very intense absorption at 1308 and 1282 cm^{-1}, corresponding to vibration of carbonyl-substituted aro-

matic nuclei, and an absorption band at 1080 cm^{-1}, which should be assigned to antisymmetric stretching of the phenyl−S group.[41] Absorption bands at 849 and 828 cm^{-1} are attributed to out-of-plane bending of the ring C−H bonds.

Interestingly, the IR spectrum of monomer **2** is similar to that of polymer **2a**. The difference mainly relates to the carbonyl absorption band, which is observed at 1649 cm^{-1}, and two bands at 1086 and 1071 cm^{-1} (instead of one band at 1080 cm^{-1} in the polymer).

As mentioned above, polymer **2a** obtained after dynamic heating to 480 °C was insoluble. In attempts to a obtain a soluble product, we performed isothermal heating of the sample in the temperature range 335−380 °C, i.e., the range used mainly for both catalyzed and uncatalyzed ring-opening polymerizations of arylene thioether and arylene thioether ketone macrocycles. Heating sample **2** at 335 °C for 40 min produced a partially soluble material containing a significant amount of the initial macrocycle (DSC analysis showed a sharp melting peak 327 °C). Thermal treatment of the sample at 360 °C for 40 min and at 380 °C for 20 min also resulted in partially reacted material. There was no evidence of the presence of starting dimer **2** after heating at 380 °C for 30 min. However, all of the products obtained were insoluble. Therefore, branching seems to occur simultaneously with polymerization.

Heating the cyclic oligomer mixture **7** (2 < *n* < 16)
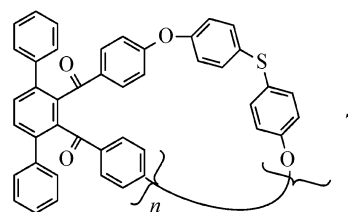
in the absence of catalyst at 380 °C for 30 min in the melt led to the formation of high molecular weight polymer, with 33% cyclics remaining.[23] Heating of the cyclic oligomers at 390 °C under a shear rate of 10 s^{-1} also produced high-molecular-weight polymers.[27] Clearly, the thermal behavior of the single-sized macrocycle **2** cannot be compared directly with that of the macrocyclic mixture described by Hay et al..[23,27] However, one can speculate that the difference in the reactivity of these two materials under isothermal heating conditions should not be very large.

To gain further insights into the polymerization mechanism and structures of the products obtained under dynamic heating, an alternative approach is to use monomers, which lead to semicrystalline or crystalline ordered polymers. In this context, macrocycles **3** and **4**, which contain para-substituted fragments, are promising candidates for studies. The DSC scan of trimer **3** is presented in Figure 6. A sharp melting peak observed at 449.5 °C (curve A), and, quite similar to dimer **2**, fine crystalline powder **3** transforms into tough material after the heating scan.

The second DSC scan (B) is typical for semicrystalline polymers quenched from the melt—a well-resolved glass transition and approximately equal peaks of cold crystallization and melting.

Polymer **3a** after the first heating scan was completely soluble in strong acids, such as concentrated sulfuric acid and a mixture of methanesulfonic acid with methylene chloride or chloroform.
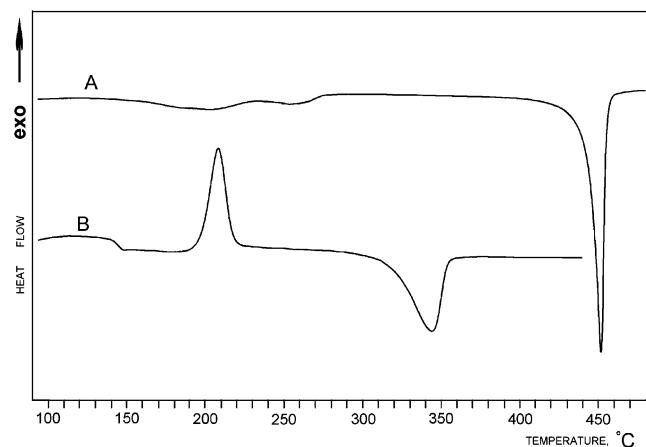
Figure 6. DSC traces of macrocycle **3**: (A) first scan; (B) second scan.

The good solubility of polymer **3a** permitted its structural study by NMR spectroscopy. An important part in these studies is evaluation of monomer (macrocycle) conversion into polymer. Very often ring-opening polymerization of macrocycles, carried out in the melt, occurs with a significant amount of monomer remaining unreacted. It is believed that the later stage of the polymerization experiences a highly viscous condition under which diffusion of unreacted macrocycles toward reaction centers is retarded. Figure 7 presents ^{1}H NMR spectra of monomer **3** and polymer **3a.** Because of the insolubility of polymer **3a** in a mixture of deuterated chloroform with trifluoroacetic acid, a mixture of methanesulfonic acid with deuterated chloroform and small amounts of trifluoromethanesulfonic acid was used for preparation of the solutions.

The spectra are well resolved. Signals of macrocycle **3** are somewhat broadened in a comparison with those in a solution of chloroform and trifluoroacetic acid, Figure 1.) Signals of protons for macrocycle **3** and polymer **3a** appeared at 7.89, 7.64 ppm and 7.92, 7.62 ppm, respectively. Spin−spin coupling constants are 8.35 and 8.46 Hz. The ^{13}C NMR spectrum of **3a** is also very well resolved, and a number of signals corresponding to those expected for the repeating unit were observed:

An important conclusion from the NMR studies is that the NMR spectra of **3a** do not reveal signals which might be attributed to the presence of residual monomer in the polymer. Another conclusion is that polymer **3a** does not consist of any appreciable amount of defect structures. Unfortunately, the insolubility of polymer **3a** in common organic solvents did not allow for GPC measurements to be performed. However, reprecipitation of polymer **3a** from a solution in MSA/CHCl$_3$/TFSA mixture into methanol followed by intensive washing with hot methanol in a Soxhlet extractor showed practically quantitative recovering (98%) of the polymer, and, therefore, absence of the initial macrocycle.

Heating scans were performed at 20 °C/min. Therefore, it is easy to calculate that polymerization, started after melting of the macrocycle at 450 °C, proceeded over 3−3.5 min (taking into account that cooling from 480 to 350 °C takes approximately 2 min). It is, therefore, very likely that the heating rate would affect polymerization strongly. Two heating scans of monomer **3** were performed at 15 and 10 °C/min. ^{1}H NMR spectra of the resulting polymer were very similar. Viscosity data,
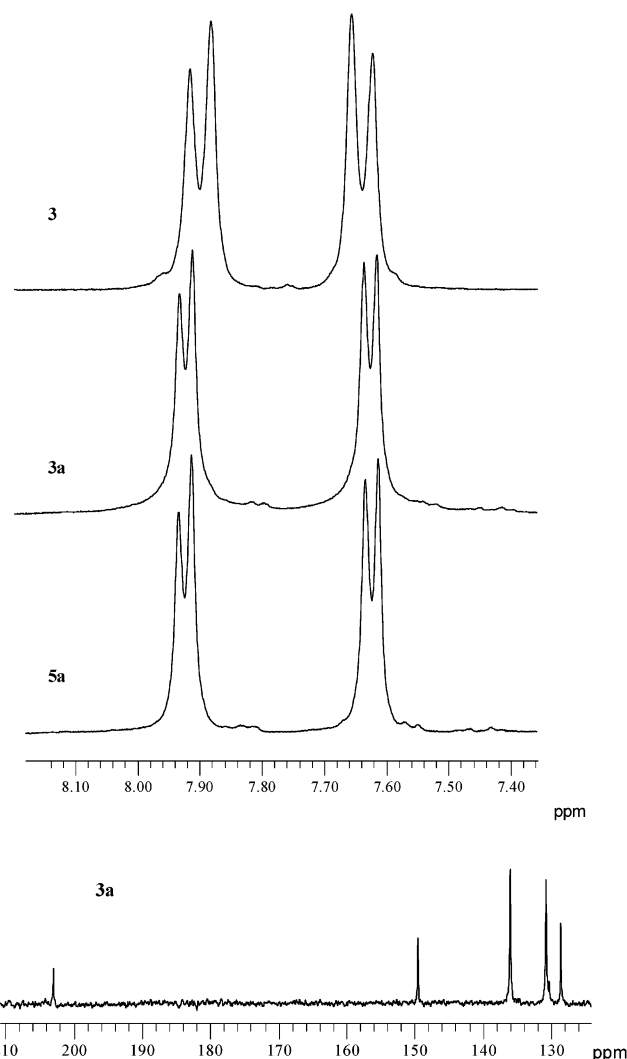
Figure 7. ^{1}H NMR spectra (aromatic region, in a mixture of CH$_3$SO$_3$H + CDCl$_3$ + CF$_3$SO$_3$H) of macrocycle **3**, polymers **3a** and **5a** (top). ^{13}C NMR spectrum of polymer **3a** (bottom).

Table 1. Viscosity Data of the Polymers

polymer	heating rate,°C/min	η_{inh} (dL g^{-1})^b
3a	20	0.73
3a	15	1.06
3a	10	1.05
5a^a		0.92

^{a} Polymer **5a** was obtained by solution polymerization in diphenyl sulfone solution. ^{b} In H$_2$SO$_4$.

measured for the 0.2% solutions of polymers in concentrated sulfuric acid, are given in Table 1.

Indeed, a decrease in the heating rate increases the viscosity values, which, in fact, correspond to optimal viscosity values for semicrystalline engineering thermoplastic polymers of the poly(arylene ether ketone) type.

The melting behavior of macrocycle **4** is very similar to that of macrocycle **3**, except that the melting peak of macrocycle **4** is observed at 439 °C, but the second scan is essentially the same, which indicates the formation of the semicrystalline product after the first heating of **4**.

As mentioned above, use of macrocyclic mixtures is widely employed in macrocyclic chemistry.[14,21,23] Therefore, after the successful polymerization of monomers **2−4**, we decided to perform dynamic-heating-induced
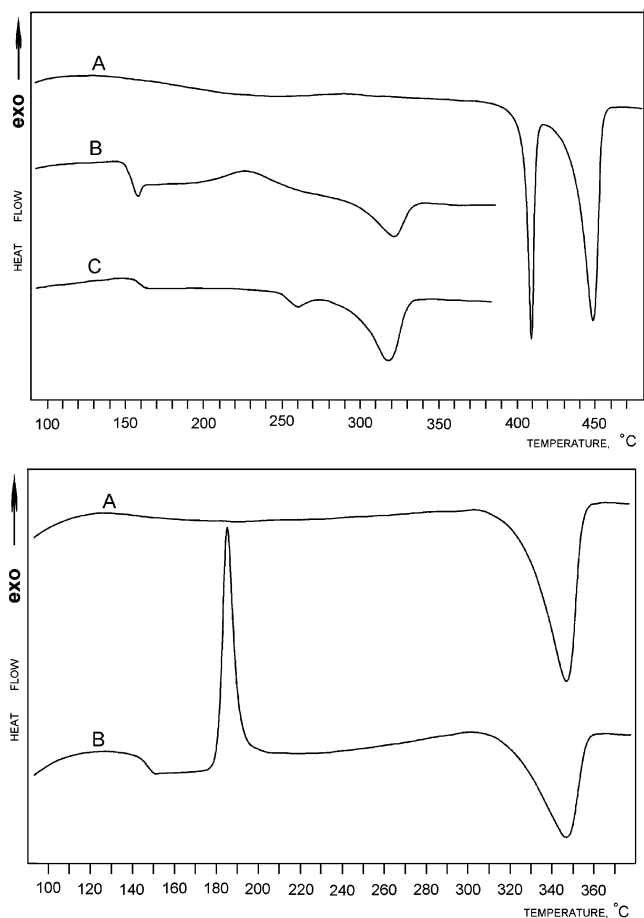
Figure 8. DSC traces of macrocycle **5** and polymer **5b** (top) and polymer **5a** (bottom).

polymerization of a mixture, **5**, of macrocycles **3** and **4**. According to DSC data (Figure 8, curves A and B), dynamic heating of **5** also results in the formation of semicrystalline polymer **5b**. The peaks of cold crystallization and melting are somewhat less intense in comparison with that of polymer **3a**. However, annealing of polymer **5b** after the first scan at 280 °C for 15 min increases its melting peak. Finally, annealing of the quenched polymer at 240 °C for 15 min results in the appearance of an additional melting peak at 258 °C; this is the so-called double melting peak, which appears in some semicrystalline polymers, such as poly(ether ether ketone)s and poly(ethylene terephthalate). Several years ago the phenomenon was a subject of intensive discussion.[42−52] Polymer **5b** is insoluble in organic solvents and acids, although it swells appreciably. The melting peak of the polymer at 320 °C is somewhat lower in comparison with those of polymers **3a** and **4a** (339 °C). Very likely, this difference in melting points originates from the less ordered, slightly cross-linked structure of polymer **5b**.

3.2.2. Catalyzed Solution Ring-Opening Polymerizations. It is obvious that comparison of polymers **3a** or **4a** obtained under dynamic heating conditions with the polymers of the same chemical structure from the catalyzed ring-opening reaction at lower temperatures would be very informative. Solution ring-opening polymerization of macrocyclic mixture **5** was carried out in diphenyl sulfone solution at 310 °C in the presence of 4% mol of the potassium salt of 9,9-bis(4-hydroxyphenyl)fluorine for 2 h. Polymer **5a**, completely soluble in concentrated sulfuric acid, was obtained in virtually

quantitative yield in 2 h. The viscosity of a solution of concentrated sulfuric acid containing 0.2% polymer was found to be 0.92 dL/g (Table 1). DSC analysis of the polymer **5a** (Figure 8) reveals its crystallinity, which is characteristic for semicrystalline polymers of this type prepared in solution of diphenyl sulfone, when postreaction processing usually includes pouring (quenching) of a hot polymer solution in diphenyl sulfone onto cold metal sheet. The second scan (B) performed for quenched polymer indicates cold crystallization and melting peaks. The melting behavior of polymer **5a** is similar to that of polymer **3a**. Particularly, glass transition and melting temperatures are the same. ^{1}H NMR spectrum of the polymer (Figure 7) is identical with that of polymer **3a**. Therefore, the structure of the polymer **5a**, obtained by the catalyzed ring-opening polymerization, is identical with that of **3a** produced by dynamic thermal heating.

A polymer with chemical composition similar to those of polymers **3a**, **4a**, **5a**, and **5b** has been also obtained by direct polycondensation of 4,4′-difluorobenzophenone and sodium sulfide in *N*-cyclohexyl-2-pyrrolidinone at 290 °C.[53]
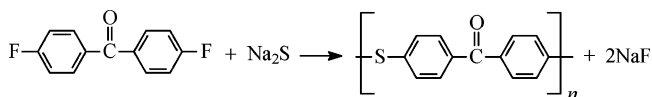

The polymer thus synthesized has viscosity η_{inh} (0.5%, H_2SO_4) = 0.90 dL g^{-1}, exhibits a glass transition at 152 °C, and melts at 335 °C; these data are very similar to those for polymers from ring-opening polymerizations.

3.3. Thermal Properties. Another way to evaluate the conversion of macrocycles under dynamic-heating-induced ring-opening polymerization conditions and characterize the thermal properties of the polymers obtained is via TGA analysis. Figure 9 shows the TGA data for compounds **2** and **5** and the polymers obtained therefrom, **2a** and **5b**. Macrocycle **2** is less thermostable than **5**. There are two degradation steps in both cases. The TGA curves of polymers **2** and **5b** indicate their essentially higher thermal stability in comparison with the initial materials. As can be seen, the dynamic-heating-initiated ring-opening polymerization of compound **5** affords tremendous improvements in the thermal stability of the final product (onset of weight loss of 0.9% is at 528 °C). For both polymer **2a** and polymer **5b**, TGA also reveals no processes which could originate from the presence of initial monomers (and their partial evaporation or decomposition). Therefore, one may speculate that full monomer conversion occurred during formation of polymers **2a** and **5b**. It is very likely that the other polymers (**3a**, **4a**, **5a**) also possess similar thermal properties.

Thus, we have shown that dynamic heating of macrocycles **1−4** leads to the formation of high molecular weight products. However, since the polymerization occurs at high temperature, a possibility of the initiation by trace impurities (in particular, by potassium salts) should be considered.

Hay reported[23] that precipitation of the DMF solution of the aryl ether thioether ketone oligomers into large excess amounts of 0.2 N hydrochloric acid followed by washing and drying affords cyclic oligomers with residual potassium ion content less than <5 ppm. We used similar treatment of reaction mixtures in cyclization syntheses, pouring filtered reaction mixture solution into diluted hydrochloric acid. Additionally, washed and
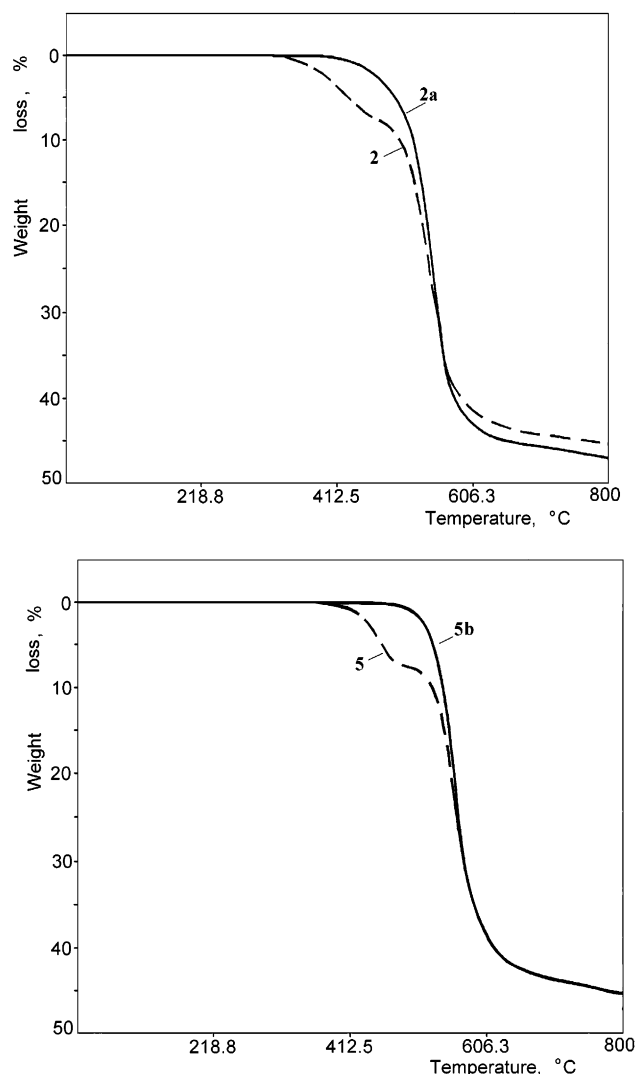
Figure 9. TGA curves of macrocycle **2** and polymer **2a** (top) and macrocyclic mixture **5** and polymer **5b** (bottom) under nitrogen.

dried products obtained (macrocycles **3** and **4**) were extracted with methylene chloride followed by recrystallization of methylene chloride extract from chlorobenzene with charcoal and chromatographic separation.

We believe that the procedure affords macrocycles of high purity. There are no reasons to assume that "nonpolymerizable" macrocycle **6** (which was not recrystallized from chlorobenzene) consists of less impurities, than rest of macrocycles, and, therefore, more stable. "Nonpolymerizabilty" of **6** also proves that metal DSC pan do not affect ring-opening polymerizations of macrocycles **1**−**5**.

For a comparison, a number of arylene ether ketone macrocycles obtained by a similar procedure was subjected to dynamic heating. For example, oxygen analogous of macrocycles **1**, **2**, and **3** showed no indication whatever of polymerization on dynamic heating to 480 °C, subsequent DSC scans simply reproducing the melting curve of the macrocycle.

Finally, good reproducibility of ring-opening reactions of macrocycles **1**−**4** and, in particular, **3** points, in our opinion, to the negligible effect of traces impurities on uncatalyzed polymerization of individual macrocyclic poly(arylene thioether ketone)s.

3.4. Mechanistic Aspects. 3.4.1. Thermolysis of Arylene Sulfide Oligomers. We believe that high-

temperature transformations of cyclic arylene thioether ketones under dynamic heating conditions have not been previously reported. Therefore, to clarify the reaction mechanism, it would be useful to consider briefly the thermoinitiated processes in linear poly-(arylene sulfide)s, which have received significant attention mainly because of the successful commercialization of poly(phenylene sulfide) (Ryton PPS).

1,4-Arylene sulfide oligomers heated at about 370 °C may undergo polymerization (ref 54 and references cited therein). The reaction proceeds at reasonable rates at 300−395 °C and is promoted by air or phenyl disulfide. It is almost totally inhibited by a free-radical trap such as 2,6-di(*tert*-butyl)-4-methylphenol, which indicates its free-radical nature. A mechanism has been suggested that involves homolytic scission of C−S bonds to provide thiyl and aryl free radicals.[54] The thiyl radicals are postulated to attack the carbon end of the group and repeat units alternately
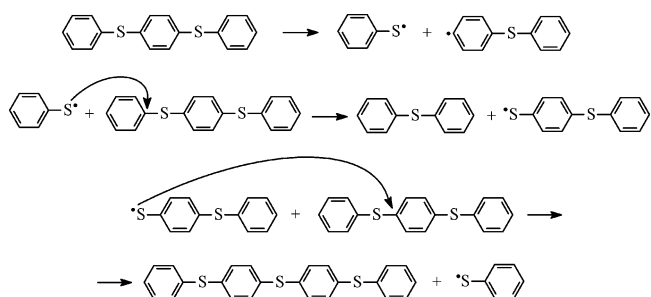
The mechanism suggests a dynamic equilibrium with para−yielding only para-catenation. Taking into account the high temperature of the reaction, the observed selectivity is noteworthy.

Similar results were obtained when the oligomerization reaction was applied to 1,3-bis(phenylthio)benzene, and scrambling of linkage patterns on benzene rings during the oligomerization was not observed. Oligomers with mixed meta- and para-linkages were obtained from an oligomerization of a mixture of 1,3- and 1,4-bis-(phenylthio)benzene.

Further, disproportionation of unsymmetrical aryl sulfides occurred at elevated temperatures. When 4-biphenylylphenyl sulfide was heated in nitrogen at about 360 °C, two new cross-products and remaining starting material were present in ratios approaching 1:1:1.
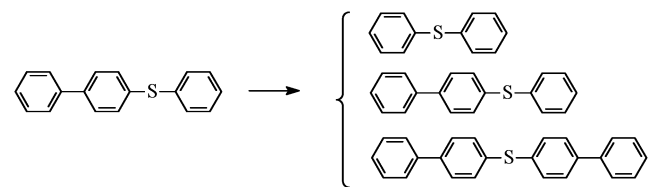
Finally, depending on the conditions (temperature; inert atmosphere or air) thermolysis of the arylene sulfides may result in the evolution of volatile substances, such as hydrogen sulfide, hydrogen, sulfur dioxide, and organic materials not present in the starting materials.

Superposition of the processes described may very likely take place, and the thermal behavior of macrocyclic compounds may differ from their linear analogues. Because of the lack of information related to noncatalyzed ring-opening polymerization of aromatic cyclic thioether ketones, and in an attempt to gain deeper

Scheme 1
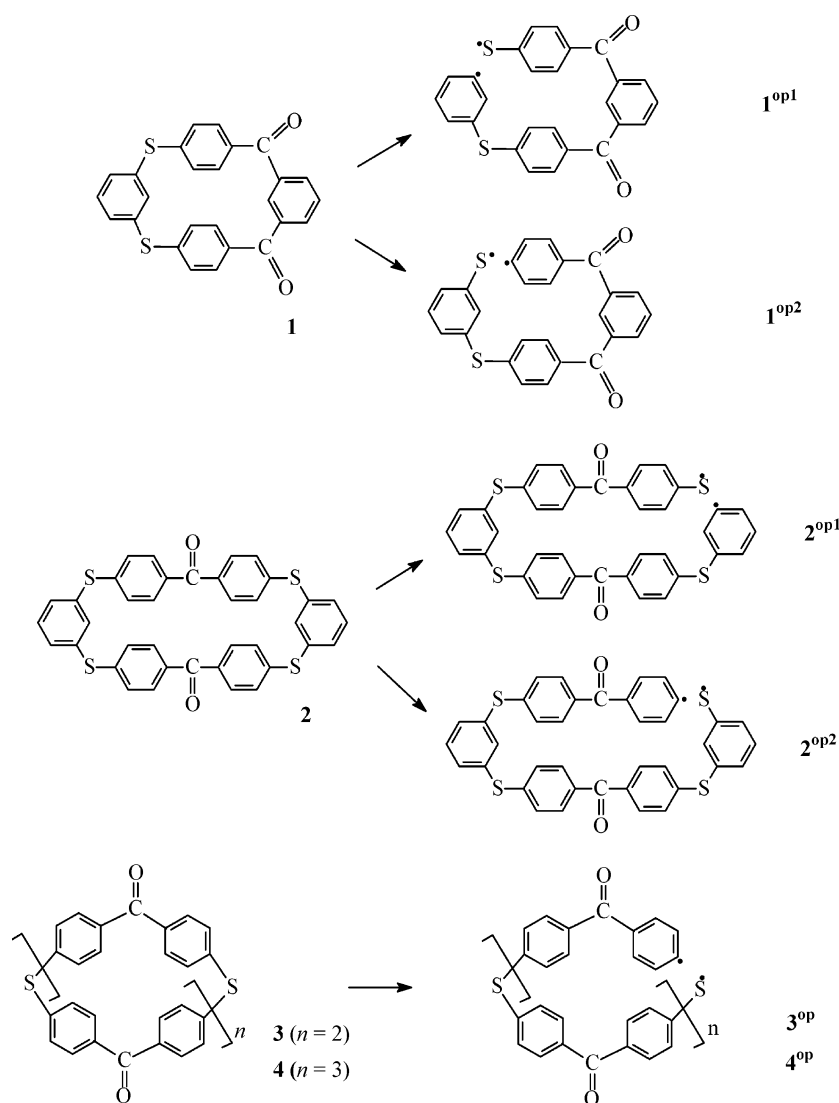
insight into the reaction mechanism, we turned our attention to molecular modeling.

3.4.2. Molecular Modeling. We used quantum mechanical calculations to evaluate the first step of the polymer-forming reaction—opening of the macrocycles. It is reasonable to suggest that ROP of S-containing macrocycles starts with homolytic dissociation of the relatively weak C–S bond. This mechanism was also proposed by Hay.[21,23.] All the structures resulting from ring-opening of macrocycles **1**–**4** are given in Scheme 1. Since macrocycles **1** and **2** can form two different biradicals due to two types of C–S and C–O bonds, respectively, each possibility has been taken into account.

To estimate the thermodynamics of the ring-opening via homolytic cleavage of the C–S bond, both cycles and opened chain triplet biradical were optimized at B3LYP/6-31G* level of theory which is known to produce reliable geometries and energies for organic molecules.[55] As can be seen from Table 2, the ring opening has positive entropy for all cycles, which facilitates this reaction with increasing temperature. Table 2 shows that all cycles show similar total electronic energies of the ring opening in agreement with their similar reactivity suggesting that this step is rate-determining. Since all cycles possess similar entropies of ring opening

Table 2. Energies (*E*), Entropies (Δ*S*), Enthalpies (Δ*H*), and Free Energies (Δ*G*) for Homolytic Ring Opening for the Studied Cycles Calculated at B3LYP/6-31G* Level at Different Temperatures

macrocycle	temp, °C			
	25	175	325	475
1				
E		70.1 (70.1)[a]		
ΔS (cal/mol)	5.7 (15.4)[b]	4.8 (12.0)	4.0 (11.1)	3.4 (10.9)
ΔH (kcal/mol)	67.4 (68.0)	67.1 (68.0)	66.7 (67.9)	66.2 (67.7)
ΔG (kcal/mol)	65.9 (64.6)	64.9 (62.9)	64.6 (61.2)	63.7 (59.6)
2				
E		69.3 (70.0)[a]		
ΔS (cal/mol)	15.2 (14.2)[a]	15.7 (14.7)	16.0 (15.0)	16.1 (15.2)
ΔH (kcal/mol)	68.5 (69.0)	68.8 (69.2)	68.9(69.3)	68.9 (69.4)
ΔG (kcal/mol)	63.9 (64.7)	61.6 (62.5)	59.2 (60.3)	56.9 (58.1)
3				
E		69.0		
ΔS (cal/mol)	13.5	14.0	14.3	14.5
ΔH (kcal/mol)	67.9	68.2	68.3	68.4
ΔG (cal/mol)	63.9	61.8	59.7	57.5
4				
E		66.3		

[a] Formation of **1op2** intermediate. [b] Formation of **2op2** intermediate.

(Table 2), the differences in their reactivities are mostly due to the difference in their bond energies. Cycles **1**,

2, and **3** show very similar DH and DG for the ring-opening, which predicts similar reactivity under high-temperature ROP conditions.

As can be seen from Scheme 1, the C−S bonds of cycles **1** and **2** can dissociate in two different ways. While for cycle **2** all thermodynamic parameters are similar to one another for the two ways of bond cleavage, this is not the case for cycle **1** due to a difference in ring-opening entropy for the two pathways. This leads to a preference in the formation of intermediate **1op2** upon ring opening.

Although thermodynamic parameters are not available for the ring opening of cycle **4**, the total electronic energies are quite similar to the enthalpy and can be used to compare the reactivity of cycle **4** with those of cycles **2** and **3**. Apparently, the lower ring-opening energy for cycle **4** is related to the additional strain energy in this cycle.

Biradicals **2op**−**4op**, formed after the first ring opening, still contain C−S bonds, which potentially may undergo further homolytic scission reactions. Similar energy calculations, performed for biradical **3op**, have shown that the dissociation of any C−S bond in biradical formation requires some 72−73 kcal/mol at B3LYP/LACVP* level, independent of the C−S bond type, which is more than the ring opening of cycle **3** itself (69 kcal/mol). This difference is probably due to ring strain release up on ring opening.

Thus, the calculations agree with the free-radical mechanism of high-temperature ROP, which shows that the bond dissociation energy determines the reactivity of the macrocycles.

3.4.3. Reaction Mechanism. Structural studies of the products obtained have shown unambiguously that ring-opening polymerizations of macrocyclic aromatic thioether ketones under dynamic heating conditions result in high-molecular-weight, linear polymers that, depending on the structure, are soluble or slightly cross-linked. NMR investigations of soluble polymer **3a** revealed no indications of structural irregularity (for example, formation of disulfide or biphenylyl units, etc.). On the other hand, the literature data considered above confirm the possibility of highly selective thermoinitiated radical processes in poly(arylenesulfide)s. The occurrence of radical homolytic ring-opening also agrees with calculations performed for the macrocycles. It is logical, therefore, to suggest the following mechanism for the uncatalyzed ring-opening polymerization of the macrocycles. Macrocycle **3** is used as an example (Scheme 2).

A homolytic scission of the C−S bond in macrocycle **3** leads to the formation of a biradical with thiyl and phenyl radicals as end groups. It is very likely that the difference between C−S bond dissociation energy in the macrocycle and linear products controls the selectivity of the polymer-forming reaction. The thiyl radical attacks a carbon atom of another macrocycle and displaces another reactive thiyl radical. Repetition of the process results in a polymer **3a** with (ideally) phenyl and thiyl end groups. It is obvious, however, that the highly reactive phenyl radical would react either with another radical or with aromatic nuclei. Apart from radical recombination or arylation reactions, processes such as recombination (cyclization) of the radicals or backbiting processes, which might lead to large macrocycles, may also occur.

As mentioned above, macrocycles **1**-**4** contain as reactive fragments sulfur atoms alternating with carbonyl groups. It is supposed[25] that, for the cyclic arylene ether thioether ketone oligomers containing a 1,2-dibenzoylbenzene moiety, the thioether linkage is activated by the electron-withdrawing carbonyl group. Therefore, one might expect that macrocyclics in which thioether linkages alternating with electron-donor ether groups would be less reactive. Even so, it is remarkable that macrocycle **6**, the structure of which was confirmed unambiguously by X-ray structural analysis, after the first scan up to 510 °C at a heating rate of 10 °C /min remained with most of the initial material still unreacted (Figure 10). A product after the fist DSC scan was fully soluble in concentrated sulfuric acid, but viscosity measurements gave value close to 0.

Homolytic dissociation energies of C−S bonds calculated for **6** at B3LYP/6-31G* level[55] are similar to those of macrocycles **2** and **3**. The calculations carried out for homolytic bond dissociation of cycle **6** at the same level of theory gave the results similar to those for cycles **1**−**3**. Assuming that the entropies of the ring opening for all these cycles are similar, one can suggest the following explanation for the low reactivity of cycle **6**: cycles **1**−**4** have more than one S atom; therefore, they are able to form separate fragments by breaking more than one C−S bond so that the probability of their recombination to re-form the cycle is low. On the other hand, in the case of cycle **6** there is only one C−S bond to break. Therefore, for macrocycle **6** there is a much higher probability of ring closure, which competes with polymerization. This situation is shown schematically as follows:
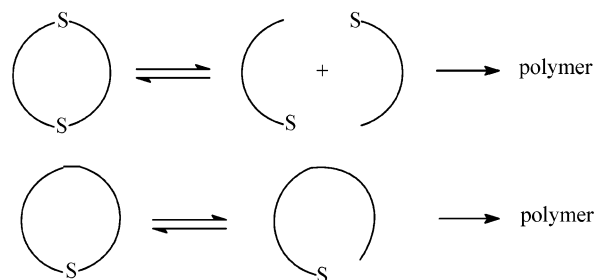

Thus, detailed investigation of the reaction mechanism of the uncatalyzed ROP also requires a study of dependence of ring−chain equilibrium on the macrocycle ring size.

4. Nanostructuring of Aromatic Thioether Ketones by Replication of Nanoporous Substrates

Because of the very high melt viscosity of commercially available high-performance materials such as polyimides, polysulfones, and polyketones, their microscale fabrication is severely limited. Processing of low-viscosity macrocycles, followed by ring-opening polymerization, was a main driving force for the majority of macrocyclic studies. Clearly, the nonisothermal polymerization of macrocyclic poly(aryl thioether ketone)s alone or in mixtures with other polymers or reinforcement additives opens up wide possibilities for their processing. Apart from that, even nanofibrils and nanotubules can be obtained from nonisothermal polymerization of the macrocycles by use of the replication method.
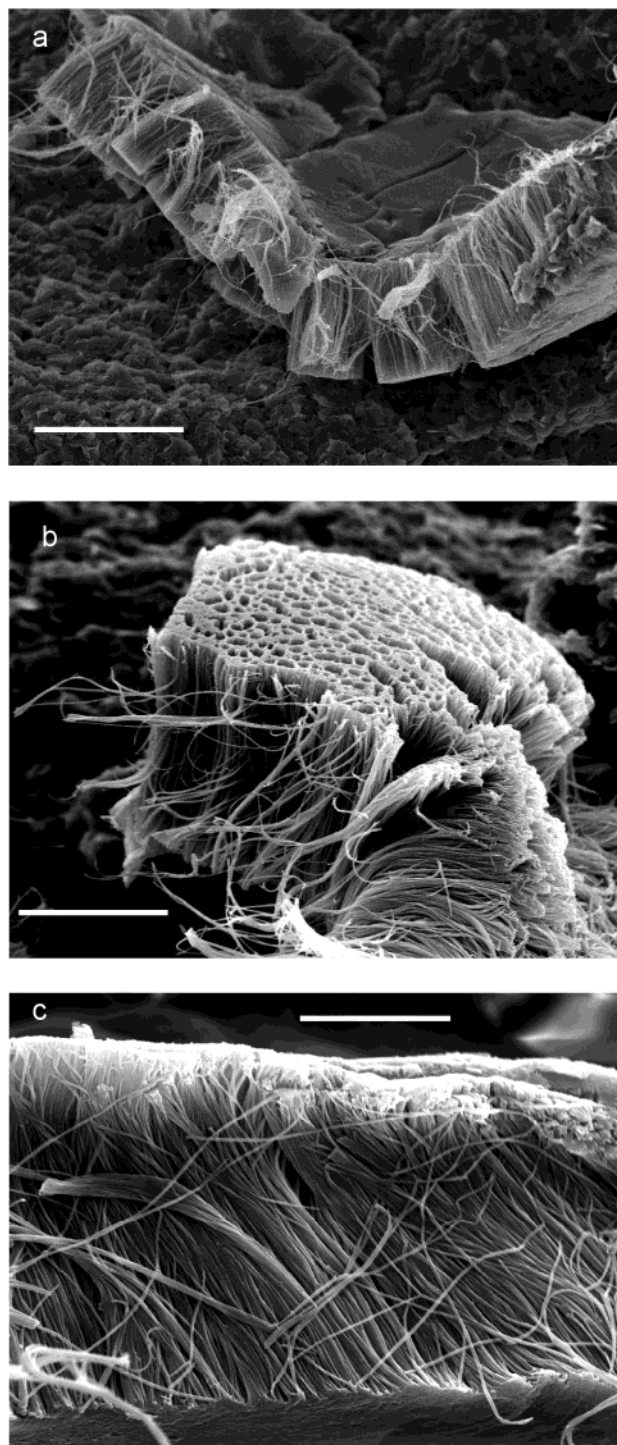
Scheme 2
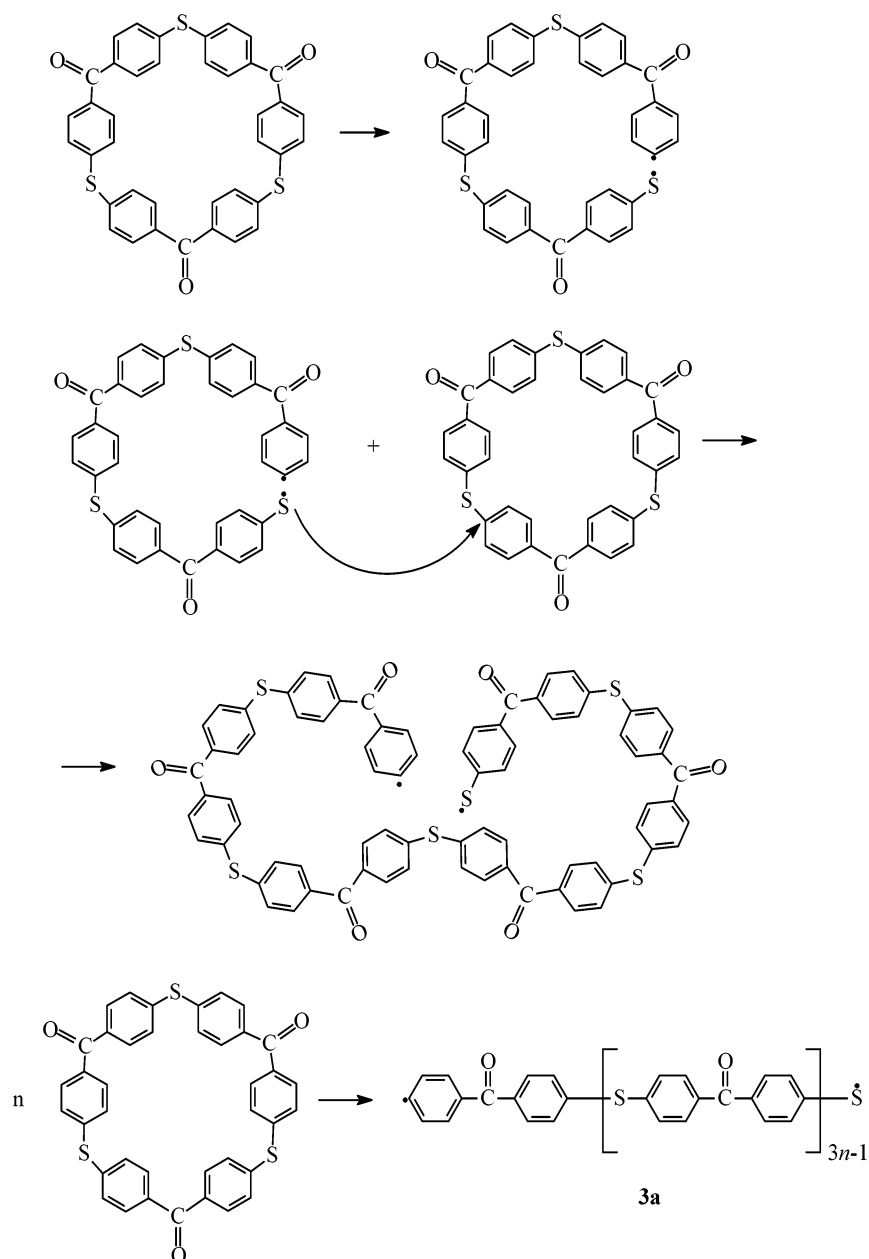
Recently, alumina membranes with parallel-running pores (whose size can be varied from ca. 5 nm up to 300 nm) were used successfully for the preparation of nanoscale-sized objects. The material of choice is deposited into these pores, and the membrane is dissolved in diluted base to give replicated structures. Preparation of inorganic, organic, and metallic nanostructures by use of alumina membranes were reported.[56−51] Very recently we have found[62] that fibrils and tubules of 200−400 nm in diameter can be produced by melt-phase, catalyzed ring-opening polymerization of macrocyclic precursors of high-performance polymers on alumina Anodiscs (Whatman). Therefore, it seemed plausible that uncatalyzed, nonisothermal polymerization of macrocyclic poly-(arylene thioether ketone)s on Anodisc would likewise produce polymeric microfibrils. Indeed, dynamic heating of Anodisc covered with macrocycles in a DSC crucible, followed by treatment with sodium hydroxide solution, washing with water, and drying, gave flexible, free-standing structures comprised of microfibrils (Figure 11). The fibrillar microstructure, extended to the full

thickness of the original membrane (60 μm) provides strong evidence that the membrane pores were completely filled by low-viscosity molten macrocycles. Flexibility of the microfibrillar structure (the Anodisc itself is brittle) and infrared spectra of membrane-formed edges taken on a spectrometer with a microfocused beam confirm its organic origin. The obvious flexibility of the resulting fibrils, which survive the processing treatment, clearly demonstrates that they are comprised of high-molecular-weight polymer and not the starting oligomer.
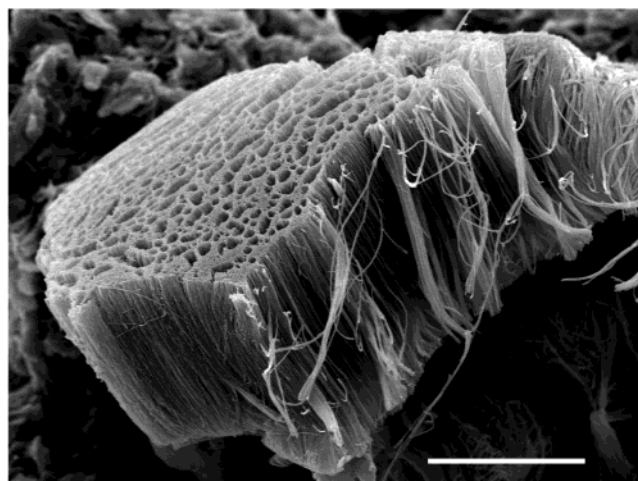
5. Conclusion

Dynamic heating of individual macrocyclic aromatic thioether ketones and their mixture results in the formation of high-molecular-weight, soluble or slightly cross-linked polymers with no residual monomer remaining. Four macrocyclic aromatic thioether ketones of different structures and a mixture of two macrocycles (**3** and **4**) were used for the studies. The heating rate significantly affected polymer properties. Depending on

Figure 11. ESM microphotograph of the membrane from polymer **3a**. Scale bar is 50 μm.

cycles and not the entropy of ring opening. The reaction mechanism proposed implies a homolytic scission of the C−S bond in macrocycles, which leads to the formation of thiyl and phenyl radicals. The thiyl radical thus obtained attacks a carbon atom of another macrocycle to form a new C−S bond and liberate another reactive thiyl radical.

Uncatalyzed ring-opening polymerization of macrocycles performed on the surface of nanoporous alumina membranes allows for fibrillar microstructures to be obtained.

It has been demonstrated for the first time that rapid, uncatalyzed, ring-opening polymerization of macrocyclic aromatic thioether ketones under dynamic heating conditions presents a promising route to new high-performance polymers for macro- and microfabrication.

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Figure 10. ESM microphotographs of the materials formed by nonisothermal polymerization of macrocycles **2** (B) and **3** (A, C). Scale bars are as follows: 75 (A), 40 (B), and 20 (C) μm, respectively.

the macrocyclic structure and heat treatment conditions, the polymers obtained were amorphous or semicrystalline, soluble, or slightly cross-linked. The structure of soluble polymer **3a** was identical with that of polymer **5a** prepared by catalyzed ring-opening polymerization in diphenyl sulfone solution, and NMR studies have revealed a high regioselectivity of polymer-forming reactions in both solution and melt. Quantum mechanical calculations are in agreement with the free-radical mechanism of ring opening, which shows that bond dissociation energy determines the reactivity of macro-

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