Macromolecules **1995,** *28,* 6371−6374 **6371**

Synthesis and Novel Free-Radical Ring-Opening Polymerization of Macrocyclic Oligomers Containing an Aromatic Sulfide Linkage

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Received April 28, 1995

Revised Manuscript Received June 23, 1995

Introduction. Ring-opening polymerization (ROP) reactions constitute an important class of polymerization reactions. The *in situ* transformation of macrocyclic oligomers such as carbonates,[1] esters,[2] aryl ethers,[3−7] aramids,[8] and imides[9] via an anionic ROP route to high molecular weight polymers opens up the possibility of melt processing of aromatic thermoplastics in applications which are currently not accessible to the corresponding high molecular polymers due to their inherent high melt viscosities.

We have been studying the cyclization[7] and ROP[10] of cyclic aryl ether oligomers containing a 1,2-dibenzoylbenzene moiety. In the course of the study of the ROP, we discovered that cyclic aryl thioether ketone oligomers **1** can be polymerized via a free-radical route to give high molecular weight linear polymers. To our knowledge, this is the first example of a catalyzed free-radical ROP of macrocylic oligomers to give high molecular weight polymers. We were interested in confirming this facile free-radical ROP of cyclic aryl thioether ketone oligomers and extending this chemistry to other cyclic aryl thioether oligomers in which the thioether linkage is not activated by an electron-withdrawing group. We were also interested in exploring a facile route for the preparation of high-performance semicrystalline thermoplastics via macrocyclic aryl thioether oligomers. A logical and simple choice of cyclic aryl thioether would be the cyclic poly(1,4-phenylene sulfide) and other aryl ether thioether cyclic oligomers, since high molecular weight poly(1,4-phenylene sulfide) is a well-known high-performance thermoplastic with excellent chemical resistance and mechanical properties. Herein, we report a synthesis of and the facile free-radical polymerization of cyclic aryl thioether oligomers.

Results and Discussion. Cyclics **1** (eq 1; Scheme 1) and **2** (eq 2) were prepared in essentially quantitative yield according to the method previously reported.[7] Cyclics **3** were prepared in quantitative yield by the chemical reduction of cyclics **2** with oxalyl chloride and tetrabutylammonium iodide (eq 3) according to the previously reported method.[13]

There are reports on the preparation and separation of the macrocyclic pentamer[11] and hexamer[12] of 1,4-phenylene sulfide (PPS). A low molecular weight polymer has been reported to form when the cyclic hexamer of PPS is heated to around its melting point.[14] Instead of preparing a discrete macrocycle, we proposed to prepare a mixture of cyclic oligomers which would have lower melting temperatures. Cyclic oligomers **4** with repeating units from 4 to 15 were prepared in high yield from copper(I) 4-bromobenzenethiolate (eq 3) under pseudo-high-dilution conditions by a modification[15] of the process reported.[12] The buildup of cyclic products can be as high as 0.070 M concentration. The mixture of cyclic oligomers was very soluble in most organic solvents, e.g., chloroform and tetrahydrofuran.

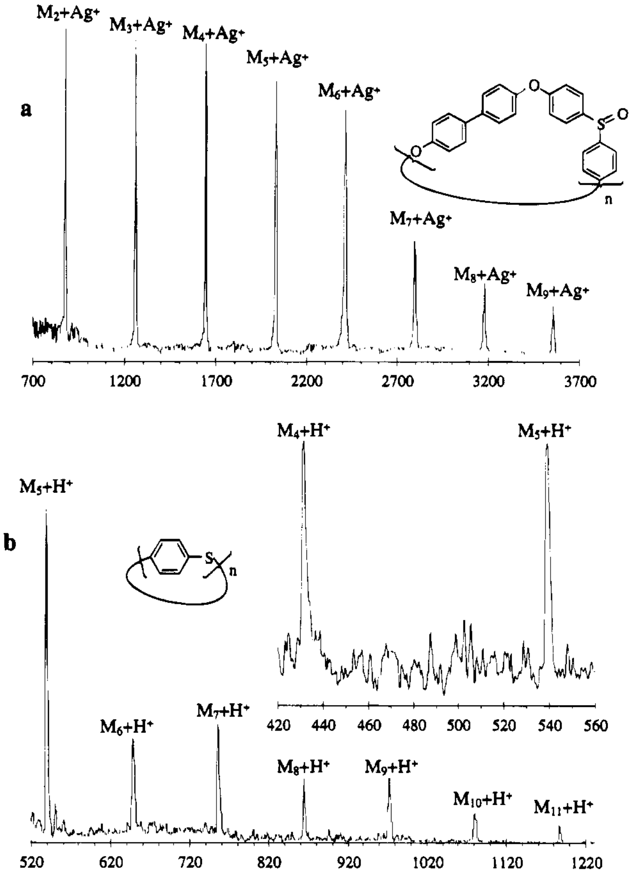

Figure 1. (a) MALDI−TOF-MS spectrum of cyclic oligomers **2**. (b) MALDI−TOF-MS spectrum of cyclic oligomers **4**.

Characterization of Cyclic Oligomers. The cyclics **1** have been fully characterized and those results will be published in a subsequent paper.[16] GPC analysis, using chloroform as the eluent and polystyrene as standards, indicates that cyclics **2** have an average degree of polymerization of about 3. ^{1}H, ^{13}C, and ^{19}F NMR spectroscopy gives no indication of the presence of any fluoro and/or phenolic end groups, which suggests that the low molecular weight oligomers are macrocyclic. Matrix-assisted laser desorption ionization−time of flight mass spectroscopy (MALDI−TOF-MS) analysis shows that cyclics **2** principally consist of macrocycles with repeating units from 2 to 9 (Figure 1a). GPC analysis shows that cyclics **2** contain 29.2% cyclic dimer, 15.4% cyclic trimer, 9.7% cyclic tetramer, 6.7% cyclic pentamer, 4.7% cyclic hexamer, and 34.3% higher homologs. The calculation was based on integration of the peak area of individual oligomers. The reduction of the sulfoxide oligomers **2** to the corresponding sulfide oligomers **3** results in a product which is not soluble in common organic solvents. Therefore, the characterization of cyclics **3** was limited. However, the quantitative reduction of similar cyclic sulfoxide oligomers to the corresponding soluble cyclic sulfide oligomers has been conducted, and the nature of the corresponding sulfide oligomers was unambiguously confirmed by a combination of MALDI−TOF-MS and ^{1}H and ^{13}C NMR.[17]

GPC analysis indicates that cyclic oligomers **4** show an average degree of polymerization of 3. MALDI−TOF-MS analysis shows that cyclics **4** (Figure 1b) principally consist of macrocycles with repeating units from 4 to 11. Reverse-phase gradient HPLC analysis of cyclics **4** was performed on a Milton Roy CM4000 pump equipped with a reverse-phase column (prime-

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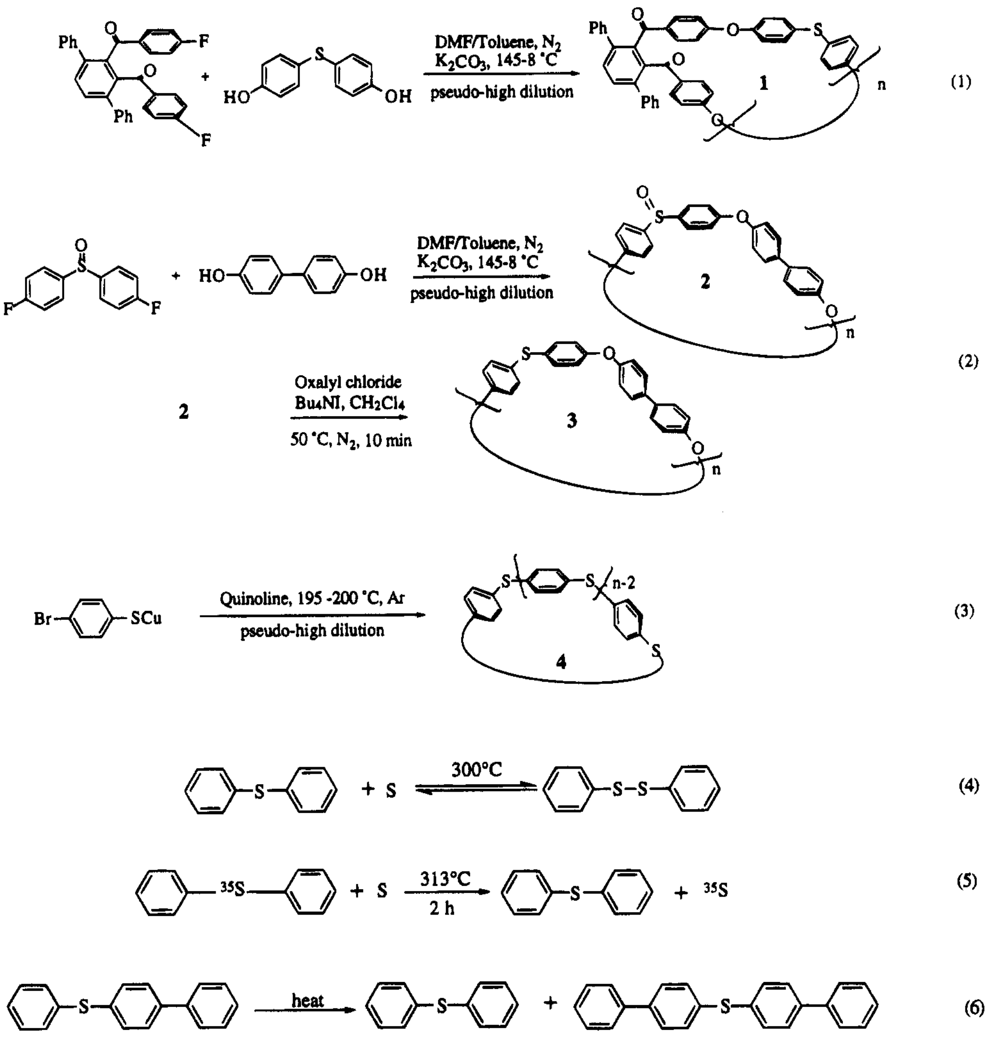
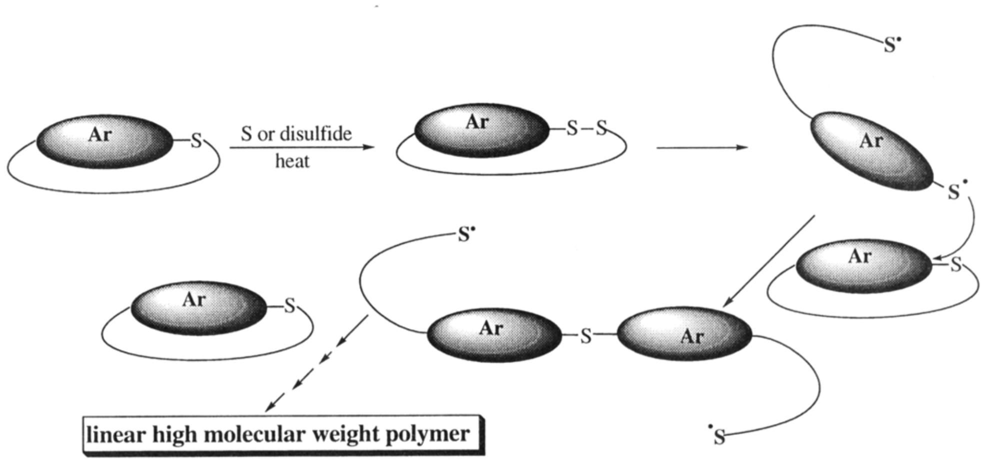
Scheme 1



sphere 5μ C8, 250 × 4.6 mm) and a UV detector at 300 nm; a THF/water gradient was used as the eluent at a flow rate of 1.0 mL/min. The gradient program was as follows: step 1, 70–85% THF over 20 min at exponent 1; step 2, 85–100% THF over 5 min at exponent 1; step 3, 100% THF for 3 min; step 4, 100–70% THF over 2 min (recycle). The analysis shows that the cyclics **4** contain 23.7% tetramer, 28.0% pentamer, 10.9% hexamer, 18.1% heptamer, 9.3% octamer, 4.9% nonamer, 2.6% decamer, 1.3% undecamer, 0.7% dodocamer, 0.3% tridecamer, and 0.1% tetradecamer. The calculation was based on integration of the peak area of individual oligomers.

DSC analyses show that cyclics **3** and **4** are highly crystalline. The DSC trace for cyclics **3** (Figure 2a) shows a melting endotherm which begins at 275 °C, has a maximum at 350 °C, and is complete at 372 °C and has a melt enthalpy change of 18.2 kJ/mol. The DSC trace for cyclic oligomers **4** (Figure 2b) shows a melting endotherm which begins at 172 °C, has a maximum at 213 °C, and is complete at 263 °C and has a melt enthalpy change of 6.0 kJ/mol. The melting temperature of the cyclic oligomers **4** is much lower than that (348 °C)[12] of a macrocyclic hexamer of 1,4-phenylene sulfide.

Free-Radical Ring-Opening Polymerization of Cyclic Aryl Thioether Oligomers. It has been known[18] for many years that sulfur reacts with diphenyl sulfide to give diphenyl disulfide (eq 4). The reverse reaction has also been demonstrated.[19] This indicates that an equilibrium exists, and this has been further demonstrated by reacting labeled diphenyl sulfide with sulfur[20] (eq 5). The thermal disproportionation of aryl sulfides (eq 6) via a radical reaction has also been reported, and the reaction can be promoted by the addition of diphenyl disulfide.[21] We have now found that heating cyclic oligomers which contain an aromatic sulfide linkage with elemental sulfur or an aromatic disulfide readily yields high molecular weight polymers by a ROP. We believe from the evidence available that this reaction proceeds via a free-radical mechanism (Scheme 2); a disulfide linkage in the cyclic oligomers may be formed by reaction of the sulfide linkage with sulfur. The disulfide moiety formed would undergo thermolysis to form thiyl radical(s) which initiate the free-radical ROP. The free-radical nature of the polymerization was confirmed by electron spin resonance spectroscopy (ESR) analysis (see Figure 3), which shows a free-radical signal centered at 3472 G. Details of the ESR analysis will be presented in another paper. In the presence of 1.0 mol % elemental sulfur, the solution polymerization of cyclics **1** in *m*-terphenyl at 350 °C under N_2 for 30 min led to the formation of high molecular weight polymer with a M_n of 18 000 and a M_w of 37 200, with 41% of cyclic oligomers remaining. The M_n and M_w were measured by GPC using chloroform as the eluent and polystyrene as standards. Extending the reaction to 3 h led to the formation of



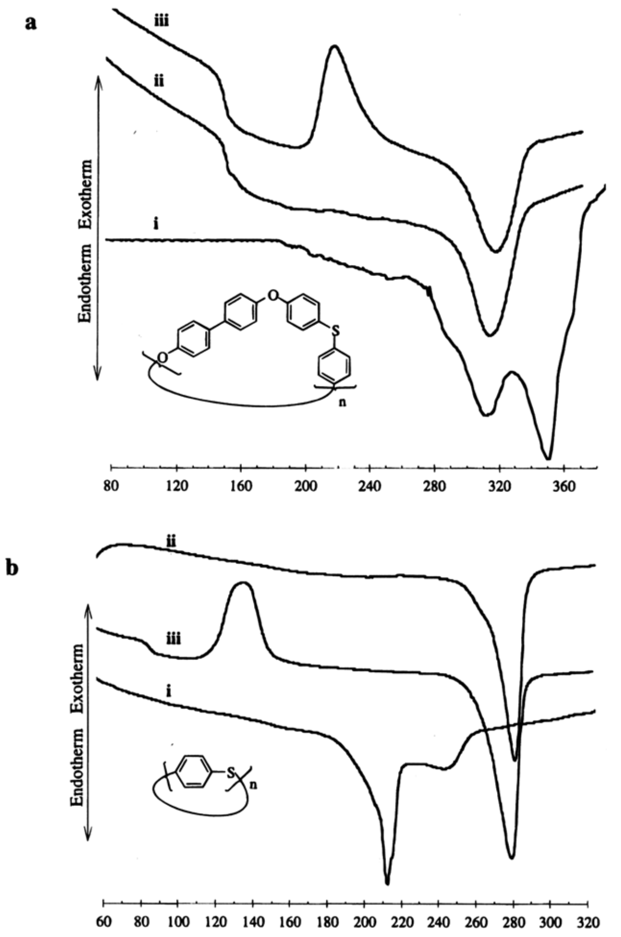


Figure 2. (a) DSC traces of (i) cyclic oligomers **3**, (ii) first scan of the resulting polymer from ROP of cyclics **3** at 350 °C under N_2 for 1 h in the presence of 1.0 mol % DTB, and (iii) second scan of ii after quenching from 370 °C on a metal block. (b) DSC traces of (i) cyclic oligomers **4**, (ii) first scan of the resulting polymer from ROP of cyclics **4** at 340 °C under N_2 for 1 h in the presence of 1.0 mol % DTB, and (iii) second scan of ii after quenching from 340 °C on a metal block.

high molecular weight polymer with a M_n of 28 200 and a M_w of 77 000, with only 9% of cyclic oligomers remaining. GPC traces of the products are presented in Figure 4a. The free-radical polymerization is different from a traditional free-radical polymerization as the molecular weight of the poly(arylene sulfide) formed depends on the reaction time and the conversion of cyclic oligomers to polymers. This is probably due to a chain equilibration among the poly(arylene sulfide) oligomers and polymers formed. The mechanism of the chain equilibration reaction should be the same as the thermal disproportionation reaction of aryl sulfides[21] via thiyl radical intermediate(s). We have observed that the reaction of the linear high molecular weight polymer analog (M_n = 33 800 and M_w = 64 800) of cyclics **1** with 2 equiv of 1-iodonaphthalene at 350 °C in *m*-terphenyl under N_2 formed low molecular weight material (M_n = 5200 and M_w = 13 000). The reaction of cyclics **1** with 2 equiv of 1-iodonaphthalene formed only low molecular weight linear oligomers. Although the reaction is complex and the products are very difficult to characterize, it may be argued that the formation of thiyl radical(s) is necessary for the reaction of arylene sulfide with 1-iodonaphthalene, as we have previously described for the reaction of aryl disulfides with iodo compounds.[22]

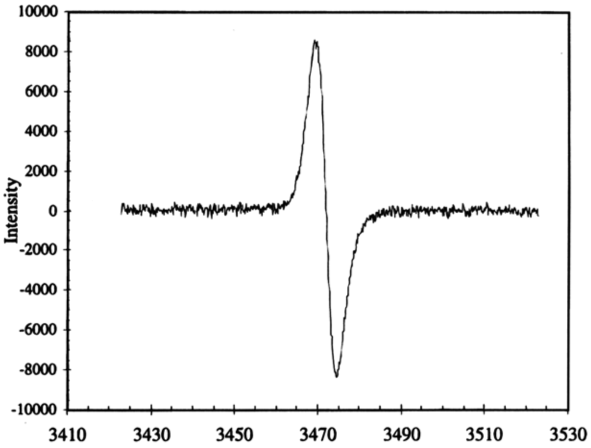


Figure 3. ESR spectrum for the reaction mixture of ROP of cyclics **1** with 4.0 mol % DTB in *m*-terphenyl at 350 °C for 1 h. The ROP was conducted in a sealed ESR tube; it was immediately shock-cooled in liquid nitrogen at the end of the reaction and stored in liquid nitrogen until analyzed. The ESR spectrum was recorded at room temperature on a Bruker ESP 300E spectrometer operating with a microwave frequency of 9.75 GHz at 2.01 mW power with a modulation frequency of 100 kHz.

The melt polymerization of cyclic oligomers **1** at 380 °C in the presence of 1.0 mol % 2,2′-dithiobis(benzothiazole) (DTB) in N_2 for 1 h led to almost complete polymerization with less than 8% of cyclic oligomers remaining. The polymer formed had a M_n of 24 500 and M_w of 103 500. The GPC traces of cyclics **1** and the resulting polymer are shown in Figure 4b. The conversion of cyclic oligomers to polymer was proportional to the concentration of disulfide DTB used. In the presence of higher concentrations of DTB (e.g., 5 mol %)

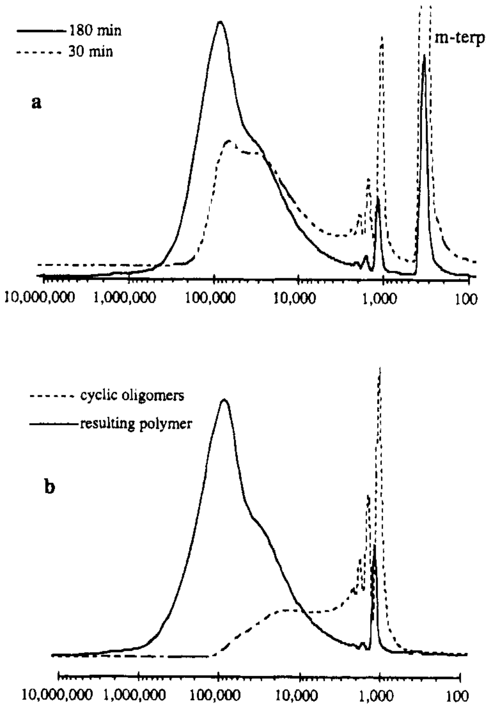


Figure 4. (a) GPC traces of the products from solution polymerization of cyclic oligomers **1** in *m*-terphenyl at 350 °C under N_2 in the presence of 1.0 mol % S for 30 or 180 min. (b) GPC traces of cyclic oligomers **1** and the resulting polymer from melt ROP of cyclic **1** at 380 °C under N_2 for 1 h in the presence of 1.0 mol % DTB.

polymerization for 30 min led to the complete conversion of cyclic oligomers to polymers which had a M_n of 8000 and M_w of 35 400.

The free-radical polymerization chemistry of cyclics **1** has been extended to cyclics **3** and **4** which do not have an electron-withdrawing group. The melt polymerization of cyclics **3** at 350 °C in the presence of 1.0 mol % DTB under N_2 led to the formation of polymer which was very tough and only partially soluble in boiling 1-chloronaphthalene. DSC analysis revealed that the resulting polymer is highly crystalline and readily recrystallizes upon heating after quenching without the need of annealing (see Figure 2a). The resulting polymer had a T_g of 150 °C and a T_m of 313 °C and a melting enthalpy change of 5.5 kJ/mol, which is comparable with those of the high molecular weight polymer reported.[13] Melt polymerization of cyclics **4** at 340 °C in the presence of 1.0 mol % DTB under N_2 led to the formation of high molecular weight poly(1,4-phenylene sulfide) (PPS) that was only partially soluble in boiling 1-chloronaphthalene. DSC analysis revealed that the resulting polymer is highly crystalline and readily recrystallizes upon heating after quenching without the need of annealing (see Figure 2b). The resulting polymer had a T_m of 281 °C and a melting enthalpy change of 5.0 kJ/mol, which is comparable with that (T_m = 285 °C) of commercial PPS.[23]

Typical Conditions for the Polymerization of the Cyclic Aryl Thioether Oligomers. Polymerization of Cyclic Oligomers 1 in Solution. Cyclics **1** (3.0 g), elemental sulfur (1.5 mg), and *m*-terphenyl (7.0 g) were mechanically mixed in a 50-mL dry test tube, equipped with a nitrogen inlet and outlet. After heating the mixture at 350 °C under N_2 for 30–180 min, the solution was cooled and dissolved in chloroform, and the resulting solution was added dropwise into a vigorously stirred large excess of methanol. A fibrous polymer was precipitated, filtered, washed several times with methanol, and then dried.

Polymerization of Cyclic Oligomers 1, 3, and 4 in the Melt. A typical polymerization procedure is as follows: cyclics **1** (2.0 g) were mechanically mixed with DTB (10.2 mg) in a 50-mL dry test tube. The test tube was sealed with a septum and heated at 380 °C under nitrogen for 1 h. The resulting polymer was removed by breaking the test tube. The polymerization of cyclics **3** and **4** were conducted in an identical manner but at 350 and 340 °C, respectively.

Acknowledgment. The authors thank the Natural Sciences and Engineering Research Council of Canada and General Electric Co. for financial support. The authors are also grateful to Dr. G. Tsagaropoulos for his assistance with the ESR studies.

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