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Free-Radical Ring-Opening Polymerization of Macrocyclic Aryl Ether Thioether Ketone Oligomers

Yi-Feng Wang, Kwok P. Chan, and Allan S. Hay*

Department of Chemistry, McGill University, Montreal, Quebec, Canada H3A 2K6

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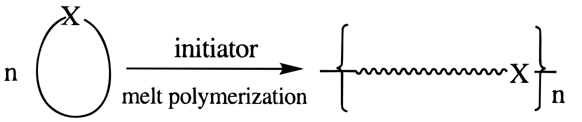
ABSTRACT: A facile free-radical ring-opening polymerization of macrocyclic aryl ether thioether ketone oligomers is described. Polymerization of the cyclic oligomers via a transthioetherification reaction to high molecular weight linear polymers is achieved both in the melt and in solution in the presence of a catalytic amount of elemental sulfur or 2,2′-dithiobis(benzothiazole) (DTB). The free-radical nature of the polymerization reaction is indicated by electron paramagnetic resonance spectroscopy (EPR). The ring-opening polymerization reaction is unusual in that the molecular weight of the polymers obtained increases as the conversion of cyclic oligomers increases. The ring−chain equilibrium dramatically favors the formation of linear polymer, in which only low levels of cyclic materials are present after polymerization, even though the reaction is not enthalpically driven. The interchain equilibration is also a facile process during polymerization. This intermolecular transthioetherification is demonstrated by using a low molecular weight arylene thioether, e.g., thiobis((phenylene-4-oxy)-4-benzoylbenzene), to control the molecular weight of the polymer formed via ring-opening polymerization.

Introduction

Ring-opening polymerization reactions (eq 1) constitute an important class of polymerization reactions.



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Using ring-opening polymerization to prepare high molecular weight polymers offers many advantages over other polymerization methods, including the elimination of the need for using solvents, the absence of volatile byproducts, and the capability of achieving very high molecular weights in a short reaction time. Many well-known polymers, such as nylon-6, silicone rubbers, polycaprolactone, and epoxides, are prepared by a ring-opening process.[1] The conventional cyclic monomers, such as epoxides and ϵ-caprolactam, are generally under ring strain, and the ring-opening polymerization is driven by the exothermic enthaply change. Since cyclic monomers such as ϵ-caprolactam have very low melt viscosity, ring-opening polymerization chemistry is very attractive for preparation of engineering thermoplastics via a reactive process, such as reaction injection molding. The attractiveness of ring-opening polymerization has driven polymer chemists to search for other cyclic monomers and/or cyclic intermediates for the preparation of high-performance aromatic thermoplastics. High-performance aromatic thermoplastics, such as polycarbonate, poly(aryl ether ketone)s, and poly(aryl ether sulfone)s, are generally prepared by condensation polymerization reactions. Conversion of the traditional monomers used in a condensation polymerization reaction to intermediate cyclic oligomers would allow processing of the low melt viscosity cyclics into high-performance aromatic thermoplastics by methods which are currently not accessible for the high molecular weight linear polymers due to their inherent high melt viscosities. This concept has led to the development and ring-opening polymerization of aromatic macrocyclic oligomers such as carbonates,[2] esters,[3] aryl ethers,[4−7] aramids,[8] and etherimides.[9] The ring-opening polymerization of macrocyclic oligomers has been achieved via anionic polymerization in the presence of initiators and driven by the entropy change as the macrocyclics have little or no ring strain. The ring-opening polymerization of macrocyclic aryl ether oligomers in the melt is generally achieved by a transetherification reaction in the presence of a nucleophilic initiator.[4−7] The most effective nucleophilic initiators include cesium fluoride,[4−7] alkali phenoxides,[10,11] and alkali benzoates.[11] Using alkali organic compounds as the initiator results in polymers containing inorganic salts and alkali phenoxide as the end groups, which is undesirable when the polymers are used in electric and electronic applications. Furthermore, the alkali phenoxide end groups would also contribute to the thermooxidative instability in the polymers at elevated temperatures.

We have been studying the cyclization,[7] ring-opening polymerization,[10,11] and rheology[12] of cyclic aryl ether oligomers containing a 1,2-dibenzoylbenzene moiety. In the course of the study of the melt stability of the cyclic oligomers, we found[12] that cyclic aryl ether thioether ketone oligomers **1**−**3** (Chart 1) are thermally unstable and undergo ring-opening polymerization to form linear high molecular weight polymers. The polymerization of cyclic oligomers **2** and **3** can be promoted by the addition of a catalytic amount of elemental sulfur or 2,2′-dithiobis(benzothiazole) (DTB) disulfide.[12] It is hypothesized that the ring-opening polymerization is initiated by the *in situ*-generated thiyl radical(s) and proceeds via a free-radical route. This hypothesis has led us to extend this novel chemistry to other macrocyclic aryl thioether oligomers in which the thioether linkage is not activated by an electron-withdrawing group.[13] The work reported here was aimed at confirming the free-radical nature of the reaction and studying the details of the ring-opening polymerization of macrocyclic aryl ether thioether ketone oligomers both in the melt and in solution. The linear poly(aryl ether ketone)s containing an unsubstituted *o*-dibenzoylbenzene moiety undergo an unknown reaction at elevated temperatures to form cross-linked networks.[11] To avoid the possible complications arising from this cross-linking reaction, cyclic oligomers **1** were chosen for these studies.

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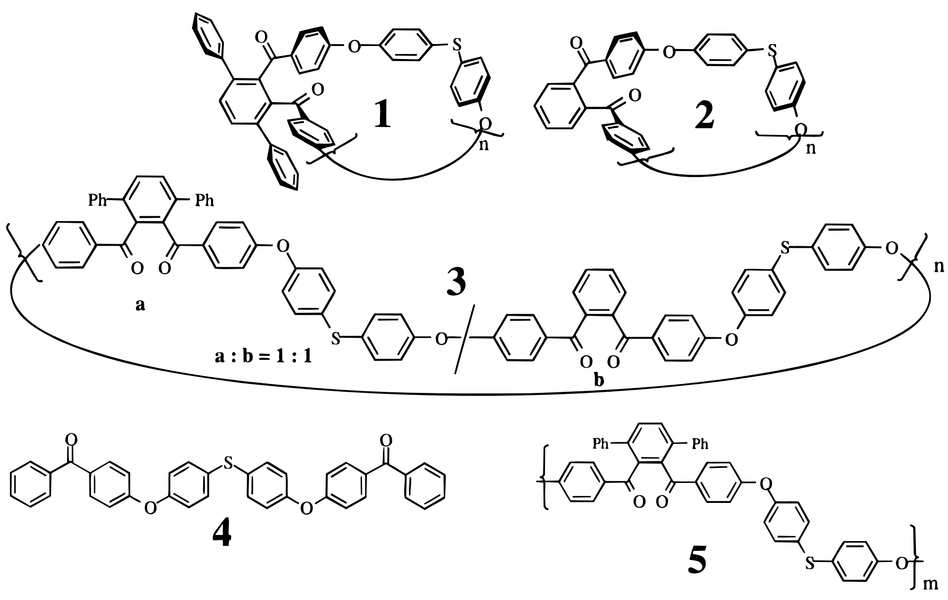
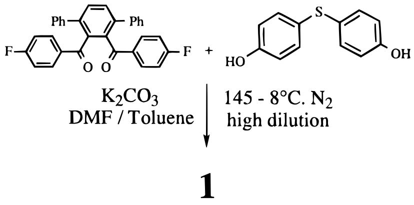
Chart 1



Results and Discussion

The macrocyclic aryl ether thioether ketone oligomers **1** were prepared by an aromatic nucleophilic substitution reaction from the potassium salt of 4,4′-thiodiphenol and 1,2-bis(4-fluorobenzoyl)-3,6-diphenylbenzene under high dilution conditions (eq 2) according to the procedure previously reported.[7,14] The cyclic nature and the compositions of **1** were characterized by a combination of ^1H and ^{13}C NMR, matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF-MS), GPC, and gradient HPLC. Details of the characterization were published in a previous paper.[14] A typical MALDI-TOF mass spectrum (Figure 1) of the cyclic oligomers **1**, using dithranol as matrix and silver trifluoroacetate as the cationization agent, gives the correct molecular ion signals for silver adducts $[M_x + Ag]^+$ of the desired cyclic oligomers, up to undecamer ($x = 2-11$), with excellent signal-to-noise ratio. Reversed-phase gradient HPLC analysis shows that the cyclic oligomers **1** were composed of 39 wt % cyclic dimer, 22 wt % trimer, 12 wt % tetramer, 7 wt % pentamer, 5 wt % hexamer, and 15 wt % higher homologues (cyclic oligomers with repeating units from 6 to 16). GPC analysis of the whole area of the curve (curve a in Figure 2) revealed that the cyclic oligomers had an M_n of 1900 g/mol and an M_w of 5700 g/mol.



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The macrocyclic oligomers **1** undergo facile ring-opening polymerization via a transthioetherification reaction at elevated temperatures under N_2 to form high molecular weight linear polymers in the presence of an initiator. The ring-opening polymerization of the cyclic oligomers **1** was conducted both in the melt and in solution using *m*-terphenyl as the solvent in the presence of a catalytic amount of DTB or elemental sulfur. The molecular weight of the formed polymers was characterized by GPC, and the conversion of cyclic oligomers to polymers was estimated on the basis of GPC measurement of the reaction mixtures. The molecular weights of the polymers formed were calculated by excluding the area of experimental curves which cover molecular weights below 3000 g/mol; in this way, the small cyclic oligomers were separated before determining the molecular weights. The structure of a typical polymer formed by ring-opening polymerization of cyclic oligomers **1** in the melt was characterized by ^1H and ^{13}C NMR spectroscopy. The free-radical nature of the polymerization was indicated by electron paramagnetic resonance (EPR) spectroscopy.

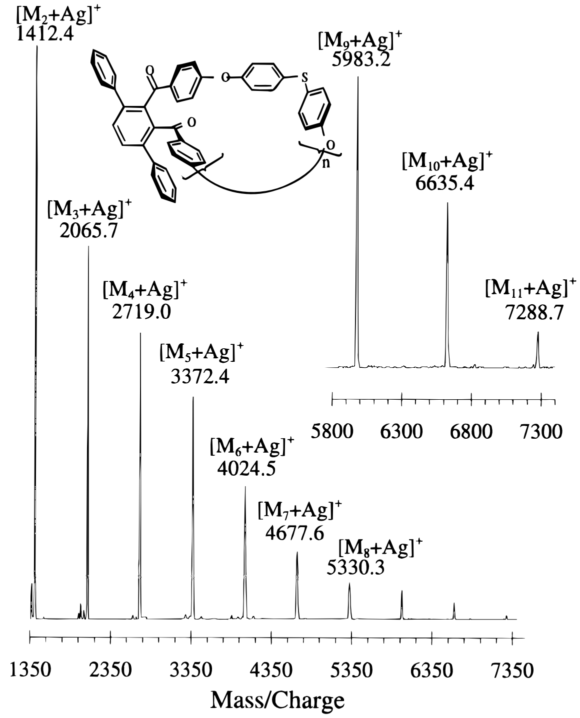
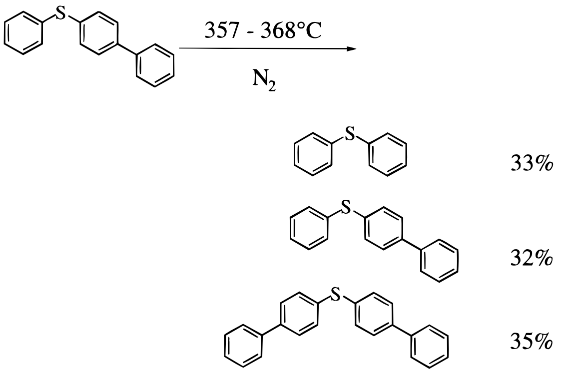


Figure 1. Positive-ion MALDI-TOF mass spectrum for macrocyclic aryl ether thioether ketone oligomers **1**. The data were acquired in the reflectron mode using dithranol as the matrix and silver trifluoroacetate as the cationization agent (dithranol/$AgCO_2CF_3$/**1** = 20:1:1 by weight).

Free-Radical Ring-Opening Polymerization of the Macrocyclic Oligomers 1 in the Melt. It was reported[5b] that, in the presence of trace amounts of potassium salts (>10 ppm), cyclic aryl ether sulfone oligomers were not stable in the melt and underwent ring-opening polymerization. However, when the residual salt was reduced below 10 ppm, the cyclics were thermally stable in the melt for a relatively long period of time. Therefore, the cyclic oligomers **1**−**3** were carefully purified to remove any residual potassium salts by precipitation of the DMF solution of the cyclics into large excess amounts of 0.2 N hydrochloric acid. Flame atomic absorption analysis indicated that the residual potassium ion content was <5 ppm. Rheological tests of the cyclic oligomers showed[12] that, although similar cyclic aryl ether ketone oligomers without a sulfide linkage were thermally stable at 350 °C in the melt for as long as 90 min, cyclic oligomers **1**−**3** were thermally unstable in the melt and underwent rapid ring-opening polymerization to form high molecular weight polymers.

In the absence of any catalyst, heating the cyclic oligomers **1** at 380 °C for 30 min in the melt led to the formation of high molecular weight polymer, with 33% cyclics remaining. A typical GPC trace of the resulting polymer is shown in Figure 2, which clearly demonstrates the formation of high molecular weight polymers upon heating the cyclics. The resulting polymer had M_n = 18 300 and M_w = 59 000. It has been reported[15] that diaryl sulfides undergo a redistribution reaction at elevated temperatures (eq 3), and it was suggested that the redistribution is initiated through the homolytic cleavage of the C−S bond to give aryl and thiyl radicals, followed by a radical aromatic substitution reaction. It is reasonable to suggest that cyclic oligomers **1** also undergo a similar homolytic cleavage of the C−S bond to form thiyl radical(s) which initiate the free-radical ring-opening polymerization, as illustrated in Scheme 1.



(3)

In an effort to confirm the free-radical nature of the polymerization, EPR spectroscopy was employed to probe the polymerization reaction mixture. Since it was not possible to carry out the *in situ* EPR experiment during the polymerization (because the spectrometer could not be operated at temperatures above 250 °C due to the limitation of the heating device), the polymerization reaction was conducted in a sealed EPR tube at 380 °C for 30 min in a preheated salt bath. At the end of polymerization, the EPR tube was immediately placed in liquid nitrogen to quench and solidify the reaction mixture. The EPR spectrum of the sample was recorded at room temperature. Measurement of *g* value was accomplished using diphenylpicrylhydrazyl (DPPH, *g* value = 2.0037) as the external reference. Typical EPR spectra obtained from the quenched polymerization reaction mixture are shown in Figure 3, along with that of elemental sulfur, which was also heated at 380 °C in a sealed EPR tube for 30 min. There is only a relatively broad and very intense singlet resonance detected for cyclic oligomers **1** treated at 380 °C (curve a in Figure 3); the measured *g* value is 2.0063 ± 0.0002. The shape of the resonance is essentially identical with that obtained from thermally treated (at 380 °C) elemental sulfur (curve b in Figure 3), which has a *g* value of 2.0066 ± 0.0002. An EPR spectrum for the mixture of cyclic oligomers **1** and sulfur (20:1 molar ratio), which was treated at 380 °C for 30 min, also shows a singlet resonance (curve c in Figure 3) with a *g* value of 2.0065 ± 0.0002. The *g* values are in good agreement with the reported *g* value of 2.0073 for a sulfur radical species

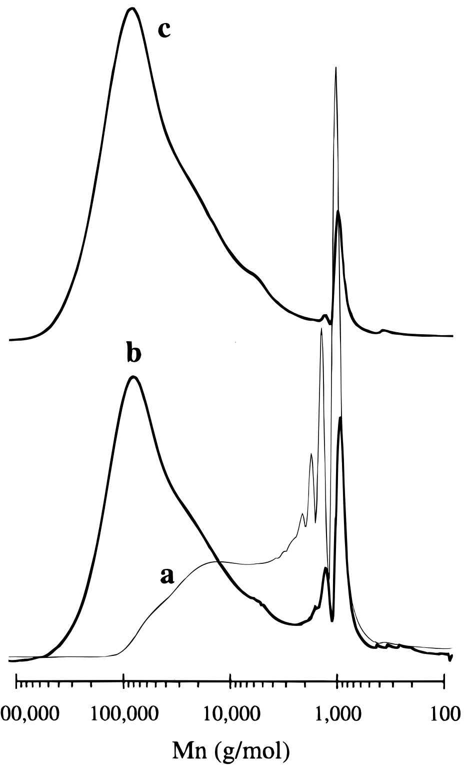
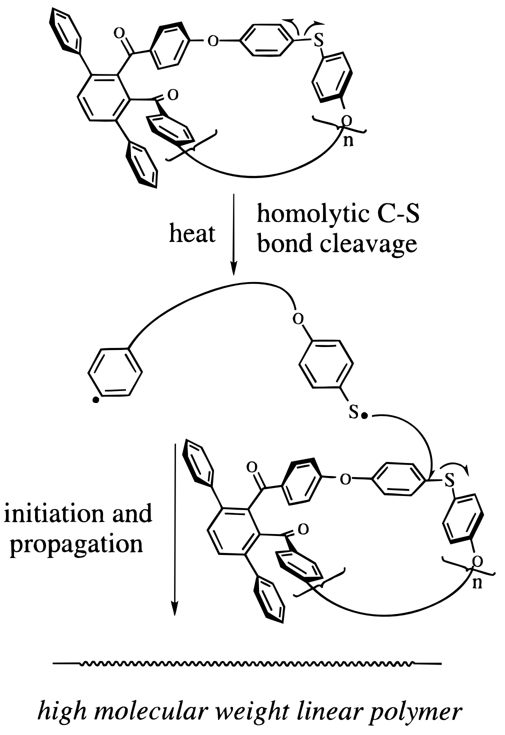


Figure 2. GPC traces of (a) macrocyclic oligomers **1**, (b) polymer resulting from heating **1** at 380 °C for 30 min, and (c) polymer resulting from ring-opening polymerization of **1** with 1.0 mol % DTB at 380 °C for 30 min.

Scheme 1



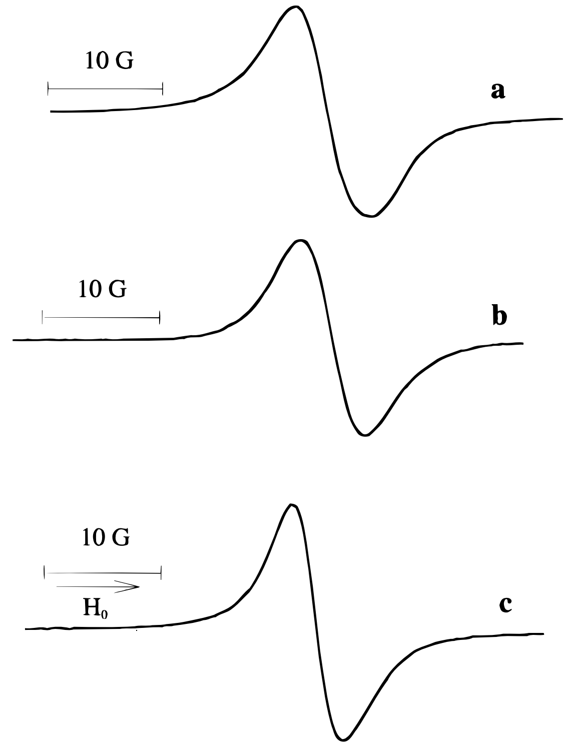
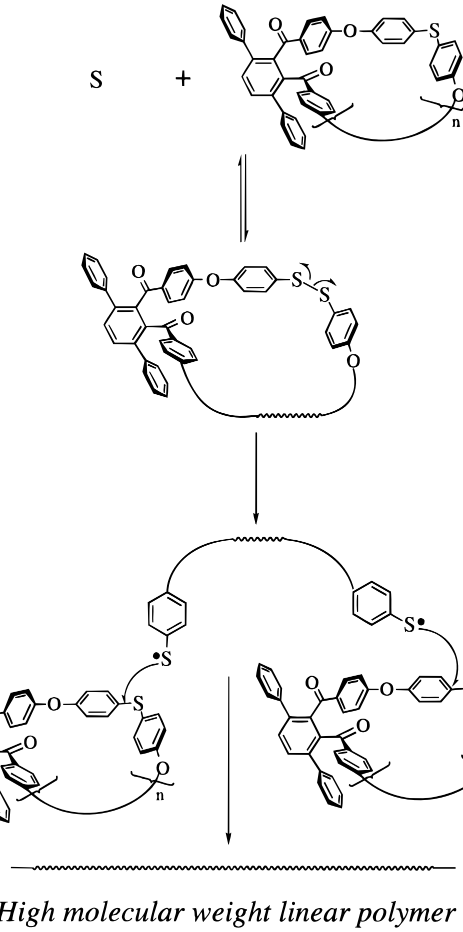


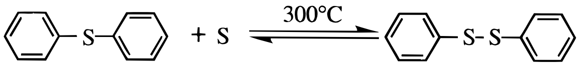
Figure 3. EPR spectra of (a) elemental sulfur after heating at 380 °C for 30 min, (b) polymer resulting from heating macrocyclic oligomers **1** at 380 °C for 30 min, and (c) mixture of reaction of the cyclic oligomers **1** and elemental sulfur (20:1 molar ratio) at 380 °C for 30 min.

Scheme 2



obtained from the reaction of *p*-diiodobenzene and sulfur.[16]

It has been known[17] for many years that sulfur reacts with diphenyl sulfide to give diphenyl disulfide (eq 4),



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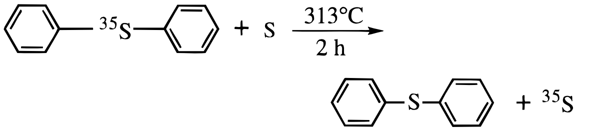
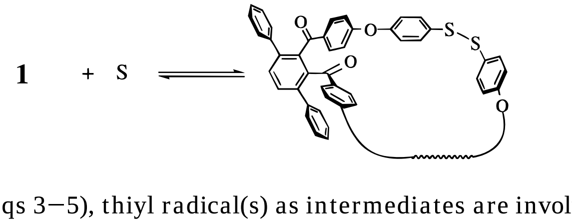
and the reverse reaction has also been demonstrated,[18] which shows that an equilibrium exists. This has been further demonstrated by reacting labeled diphenyl sulfide with sulfur[19] (eq 5). In the presence of sulfur or



(5)

disulfide, a similar equilibrium should also be feasible for the cyclic oligomers **1** (eq 6). In all these reactions



(6)

(eqs 3−5), thiyl radical(s) as intermediates are involved, and the thermal disproportionation reaction of the unsymmetrical aryl sulfide[15] (eq 3) can be promoted by the addition of diphenyl disulfide. We suspect that sulfur and arylene disulfide could also promote the ring-opening polymerization of the cyclic oligomers **1** via the possible routes illustrated in Schemes 2 and 3. Indeed, we have found that heating cyclics **1** at 380 °C with a catalytic amount of the aromatic sulfide DTB readily yields high molecular weight polymers in a relative short period of time.

When the polymerization reaction is catalyzed by the aromatic disulfide DTB, polymerization at 380 °C leads to the formation of high molecular weight polymers, with 0−17% cyclics remaining after 30 min (Table 1). In the presence of 1.0 mol % DTB, the polymerization reaction leads to polymers with only 13% cyclics present, compared to 33% cyclics remaining in the absence of DTB. The GPC trace of the resulting material is shown in Figure 2, which demonstrates that the remaining cyclics are composed predominantly of the cyclic dimer. The resulting polymer has M_n = 31 800 and M_w = 76 400. The conversion of the cyclics to polymers is proportional to the level of the disulfide DTB used (see Table 1). For example, when 5.0 mol % DTB is used, polymerization of the cyclics at 380 °C under N_2 is complete in 30 min, although the resulting material is low molecular weight polymer (M_n = 8000 and M_w = 35 400). The effect of the reaction time on the polymerization of the cyclics **1** is illustrated by the data listed in Table 2. In the initial 45 min period, 90% of the cyclic oligomers are reacted; however, over the entire 120 min period, only 93% of the cyclic oligomers are reacted. The remaining cyclics are composed predominantly of the cyclic dimer. Although there is a chain−ring equilibration among the macrocyclic oligomers and linear high molecular weight polymers, this chain−ring equilibration is much more favorable toward the formation of high molecular weight linear polymers. We speculate that the reason for the relatively large amount of cyclic dimer present after a relatively long polymerization period is the high melting temperature (>385 °C) of the cyclic dimer, which was still in the solid state

Scheme 3

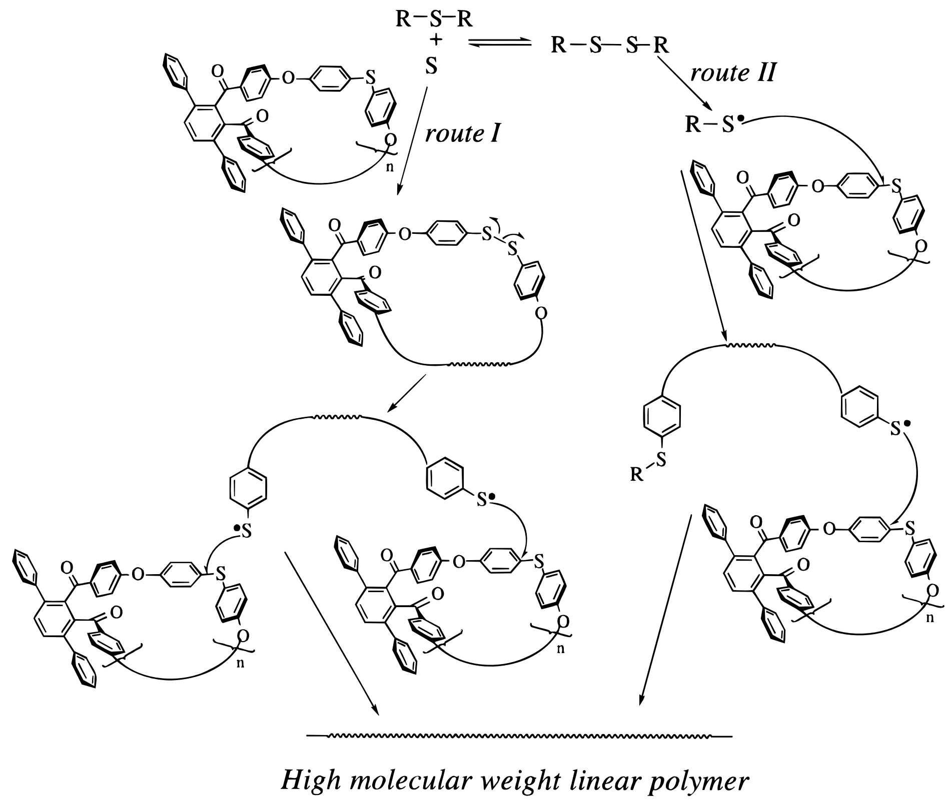


Table 1. Polymerization of Macrocyclic Oligomers 1 at 380 °C under N_2 for 30 Min Using DTB as the Initiator

initiator DTB (mol %)[a]	% cyclic remaining	$M_n{}^b$ of polymer formed	$M_w{}^b$ of polymer formed
cyclic oligomers[c]	100	1 900	5 700
0	33	18 300	59 000
0.5	17	33 700	83 600
1.0	13	31 800	76 400
2.0	9	28 200	64 500
5.0	0	8 000	35 400

[a] Molar percentage based on the repeating unit of the cyclic oligomers. [b] Measured by GPC and calibrated against polystyrene standards. [c] As-prepared cyclic oligomers.

Table 2. Polymerization of Macrocyclic Oligomers 1 at 380 °C under N_2 in the Presence of 1.0 Mol % DTB

reaction time (min)	% cyclic remaining	$M_n{}^a$ of polymer formed	$M_w{}^a$ of polymer formed	M_w/M_n
15	16.3	29 000	63 700	2.2
30	12.4	31 000	75 900	2.4
45	10.0	35 600	103 100	2.9
60	9.4	36 800	125 200	3.4
120	7.0	37 600	143 000	3.8

[a] Measured by GPC and calibrated against polystyrene standards.

at the polymerization temperature and was only partially soluble in the reaction mixture. The molecular weight of the polymers formed increases as the conversion of cyclic oligomers increases (Figure 4). This phenomenon differs from the traditional free-radical polymerization, in which the molecular weight of the polymers formed is essentially independent of the conversion of monomers. It is worth noting that the polydispersity of the polymer formed from the free-radical ring-opening polymerization increases with longer reaction times ($M_w/M_n = 2.2-3.8$) (see Table 2). This is probably due to an intermolecular chain−chain equilibration reaction. Since little or no ring strain exists in the cyclic oligomers, the transthioetherification reactions are indiscriminate with regard to cyclic or linear chain and the interchain equilibration is also a facile process during polymerization. This interchain transthioetherification will be demonstrated in a later section.

The ^1H and partial ^{13}C NMR spectra for the polymer obtained from the free-radical ring-opening polymerization of cyclic oligomers **1** at 380 °C for 120 min in the presence of 1.0 mol % DTB are illustrated in Figure 5, along with those of cyclic oligomers **1** and its high molecular weight linear counterpart **5** (Chart 1) prepared by the conventional condensation polymerization.[24] The ^1H and ^{13}C NMR spectra of the cyclics are very complex due to the large number of lines resulting from different resonances for the same atom in the repeating unit of different ring sizes. The NMR spectra of the polymer resulting from the free-radical ring-opening polymerization reactions are identical with those of the linear high molecular weight polymer **5** and no longer show the complexity of those of the cyclics.

Free-Radical Ring-Opening Polymerization of the Macrocyclic Oligomers 1 in Solution. As demonstrated in the preceding section, the cyclic oligomers **1** undergo facile free-radical ring-opening polymerization in the presence of a catalytic amount of disulfide DTB to form high molecular weight linear polymer. The ring-opening polymerization in the melt is a very fast reaction: heating the cyclic oligomers **1** at 380 °C for 15 min in the presence of 1.0 mol % DTB leads to the formation of high molecular weight polymers with an 84% conversion of cyclic oligomers. To obtain more detailed information about the polymerization behavior of the cyclic oligomers **1**, the study of the polymerization reaction at lower temperatures was desirable. We were also interested in studying the ring-opening polymerization of the cyclic oligomers using elemental sulfur as the initiator and comparing the initiation efficiency between DTB and sulfur. The cyclic oligomers **1** have a peak melt temperature of 385 °C, and elemental sulfur sublimes at that temperature; therefore, solution poly-

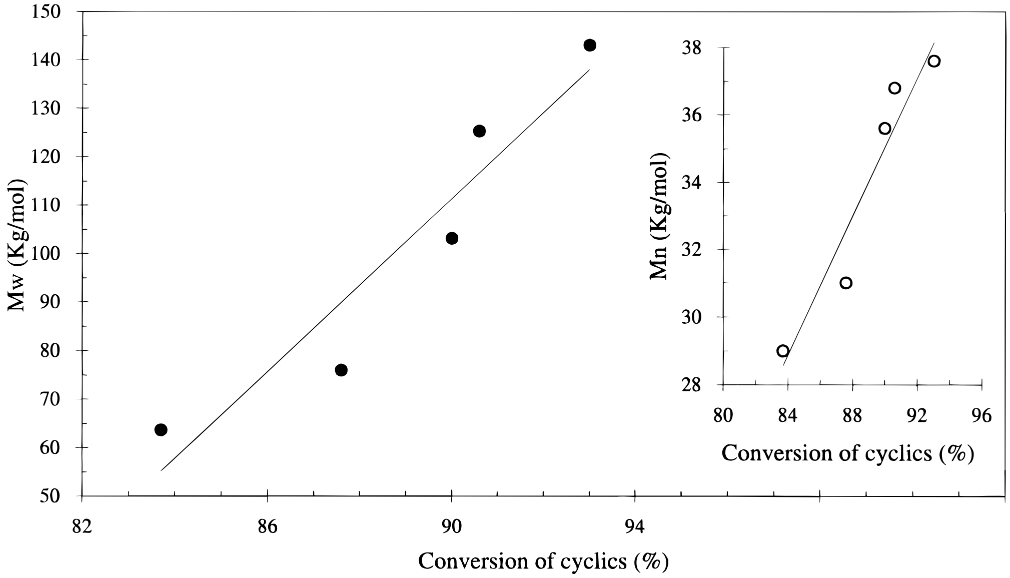


Figure 4. Dependence of molecular weights of the resulting polymers on the conversion of cyclics for the ring-opening polymerization of macrocyclic oligomers **1** with 1.0 mol % DTB at 380 °C under N_2.

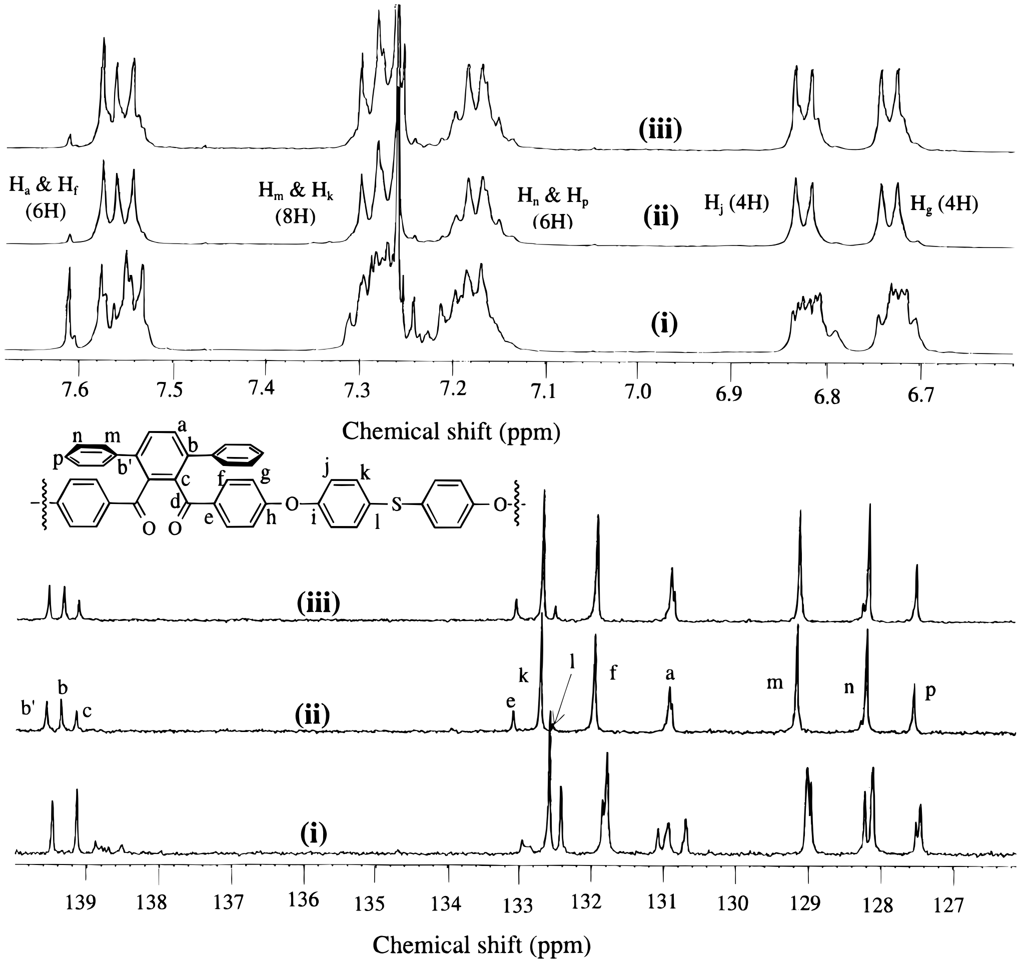


Figure 5. Partial ^{1}H and ^{13}C NMR spectra of (i) macrocyclic oligomers **1**, (ii) polymer obtained from ring-opening polymerization of **1** with 1.0 mol % DTB for 120 min, and (iii) high molecular weight linear polymer analog **5**.

merization of cyclic oligomers in the presence of elemental sulfur and disulfide DTB was conducted. The reaction was carried out in *m*-terphenyl at 350 °C under N_2 in a dry test tube sealed with a septum.

Both elemental sulfur and DTB are effective initiators for the free-radical ring-opening polymerization of cyclic oligomers at 350 °C in solution. Polymerization of the cyclic oligomers **1** in the presence of 0−5.0 mol % DTB at 350 °C for 30 min leads to the formation of high molecular weight polymers with moderate conversion (29−72%). In the presence of 0−5.0 mol % S, the polymerization reaction, under the same conditions, leads to the formation of high molecular weight polymers with higher conversion (29−81%) (Table 3). For example, in the presence of 1.0 mol % DTB, a polymerization reaction at 350 °C in *m*-terphenyl for 30 min leads to only 46% conversion of the cyclics. The resulting polymer has M_n = 15 500 and M_w = 31 000.

Table 3. Polymerization of Macrocyclic Oligomers 1 at 350 °C under N_2 for 30 Min in *m*-Terphenyl Using DTB and Elemental Sulfur as the Initiator

initiator (mol %)[a]	conversion of cyclics (%)		$M_n{}^b$ of polymer formed		$M_w{}^b$ of polymer formed	
	DTB	S	DTB	S	DTB	S
0	29	29	9 400	9 400	21 200	21 200
0.5	37	45	10 700	16 200	25 200	33 300
1.0	46	60	15 500	18 000	31 000	37 200
2.0	59	64	13 000	16 200	29 400	36 000
5.0	72	81	11 000	16 400	22 700	37 800

[a] Molar percentage based on the repeating unit of the cyclic oligomers. [b] Measured by GPC and calibrated against polystyrene standards.

Table 4. Polymerization of Macrocyclic Oligomers 1 at 350 °C under N_2 in *m*-Terphenyl in the Presence of 1.0 Mol % Elemental Sulfur

reaction time (min)	conversion of cyclics (%)	$M_n{}^a$ of polymer formed	$M_w{}^a$ of polymer formed	M_w/M_n
15	45	14 600	27 700	1.9
30	60	18 000	37 200	2.1
60	74	19 600	48 900	2.5
120	85	23 000	60 200	2.6
180	91	28 200	77 000	2.7

[a] Measured by GPC and calibrated against polystyrene standards.

However, when 1.0 mol % S is used as the initiator, polymerization under the same conditions leads to 60% conversion of the cyclics. The resulting polymer has $M_n = 18\,000$ and $M_w = 37\,200$. The results indicated that elemental sulfur is a more efficient initiator than DTB in terms of the conversion of cyclics to polymers. In an equilibrium reaction, sulfur could react directly with the cyclic oligomers to form disulfide linkages. Homolytic cleavage of the disulfide bonds could then generate radicals, which could further react as shown in Scheme 2. Disulfide DTB could function via the formation of sulfur and sulfide, with the sulfur then participating in an equilibrium reaction with the cyclic oligomers as discussed before (Scheme 3, route I). The DTB could also homolytically dissociate to radicals, which could then initiate the ring-opening polymerization reaction (Scheme 3, route II). MALDI-TOF-MS analysis of the reaction mixtures of cyclics **1** with DTB in a molar ratio of 2:1 (based on the repeating unit of the cyclic oligomers) indicates the presence of cyclics with disulfide linkages.

The effect of reaction time on the polymerization in solution was examined in the presence of 1.0 mol % S. The results show that the conversion of cyclics increases as the reaction time increases (Table 4). The free-radical ring-opening polymerization at 350 °C in the presence of 1.0 mol % S for 3 h led to the formation of high molecular weight polymers, with only 9% cyclics remaining. The resulting polymer had $M_n = 28\,200$ and $M_w = 77\,000$. A time−conversion curve for the polymerization at 350 °C in *m*-terphenyl using 1.0 mol % S as initiator is shown in Figure 6. At the initial polymerization stage (0−60 min), the conversion of cyclics increased rapidly and then gradually reached a plateau, which suggests that the reaction approaches an equilibrium which we attribute to the ring−chain equilibrium. A first-order linear relationship can be observed between the reaction time and $\ln([M_0]/[M])$ for the initial stage of polymerization (see the inset in Figure 6). Figure 7 clearly shows that the molecular weight of the polymers formed increases as the conversion of cyclic oligomers increases. This suggest that the free-radical ring-opening polymerization reaction has some characteristic features of a step-growth polymerization reaction. The polydispersity of molecular weight for the

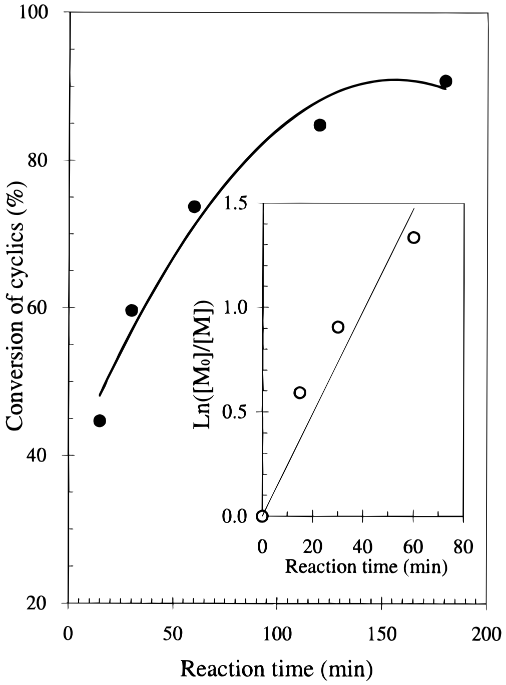


Figure 6. Time−conversion curve for ring-opening polymerization of macrocyclic oligomers **1** with 1.0 mol % S at 350 °C in *m*-terphenyl under N_2. The inset is the first-order reaction plot for the polymerization reaction in the initial 80 min.

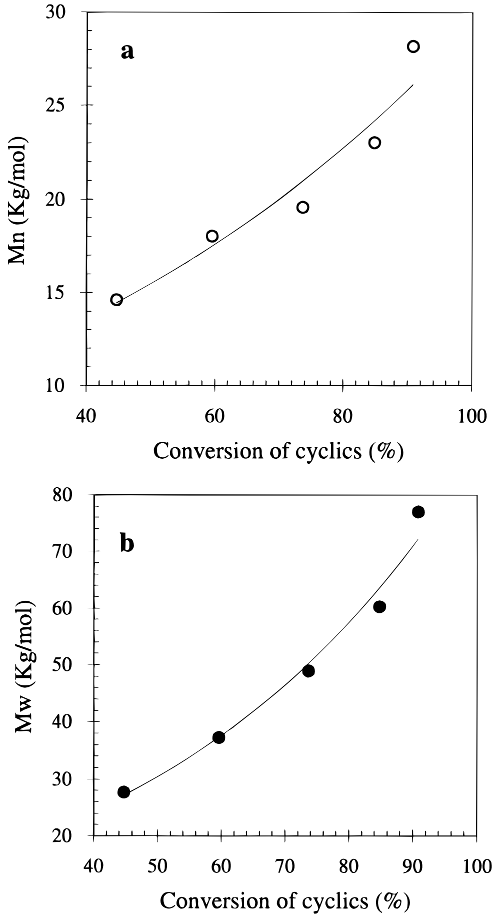


Figure 7. Dependence of molecular weights of the resulting polymers on the conversion of cyclics for the ring-opening polymerization of macrocyclic oligomers **1** with 1.0 mol % S at 350 °C in *m*-terphenyl under N_2: (a) number-average molecular weight and (b) weight-average molecular weight.

Scheme 4

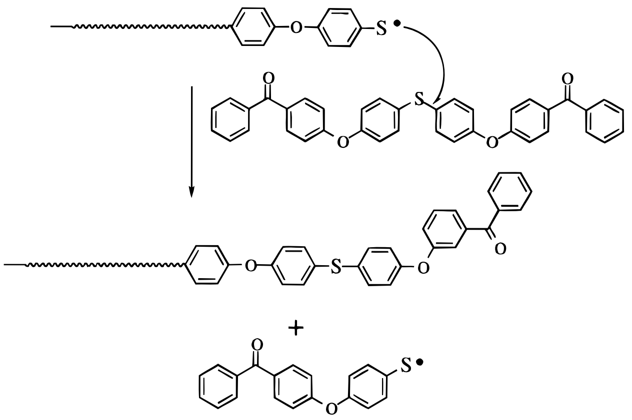


Table 5. Polymerization of Macrocyclic Oligomers 1 with 1.0 Mol % DTB at 350 °C under N_2 in *m*-Terphenyl for 150 Min in the Presence of the Chain Transfer Agent 4

chain transfer agent 4 (mol %)[a]	M_n[b] of polymer formed	M_w[b] of polymer formed	M_w/M_n
0	15 600	41 400	2.7
2.0	11 500	30 900	2.7
5.0	9 900	23 000	2.3
10.0	7 500	16 800	2.2

[a] Molar percentage based on the repeating unit of the cyclic oligomers. [b] Measured by GPC and calibrated against polystyrene standards.

polymers resulting from the solution polymerization is relatively small (1.9−2.7) compared with those (2.2−3.8) for the melt polymerization, and it also increases slightly as the conversion increases, although the change is smaller compared with those for the melt polymerization reactions (see Tables 2 and 4). The larger polydispersities of molecular weight for the polymers resulting from the melt polymerization imply that there is also a certain degree of branching which occurred at higher polymerization temperatures, and this branching becomes more apparent as the polymerization time increases. This is not unexpected, since it has previously been demonstrated[20] that poly(1,4-phenylene sulfide) (PPS) undergoes a curing reaction to form branched and cross-linked PPS when heated with sulfur.

As discussed in the previous section, since little or no ring strain exists in the cyclic oligomers, the transthioetherification reaction, which is a facile process during polymerization, would be expected to be indiscriminate with regard to cyclics or linear chains. This intermolecular transthioetherification can also be used to advantage in order to regulate the molecular weights of the polymer products. The molecular weight of the polymer may be controlled by using low molecular weight materials, such as the diphenyl aryl thioether **4** (Chart 1), as the chain transfer agent (Scheme 4). The important feature of the chain transfer mechanism is that the molecular weight is regulated by an equilibration which terminates one chain but generates an active initiation center that continues the polymerization process. In the presence of **4**, the free-radical ring-opening polymerization in solution results in polymers having lower molecular weights (Table 5). The molecular weights of the resulting polymers decrease as the level of **4** added increases. When 5.0 mol % of the aryl thioether **4** was added into the solution polymerization reaction, the reaction at 350 °C for 150 min led to the formation of a polymer which had only $M_n = 9900$ and $M_w = 23\,000$, compared to M_n of 16 600 and M_w of 41 400 in the absence of **4**.

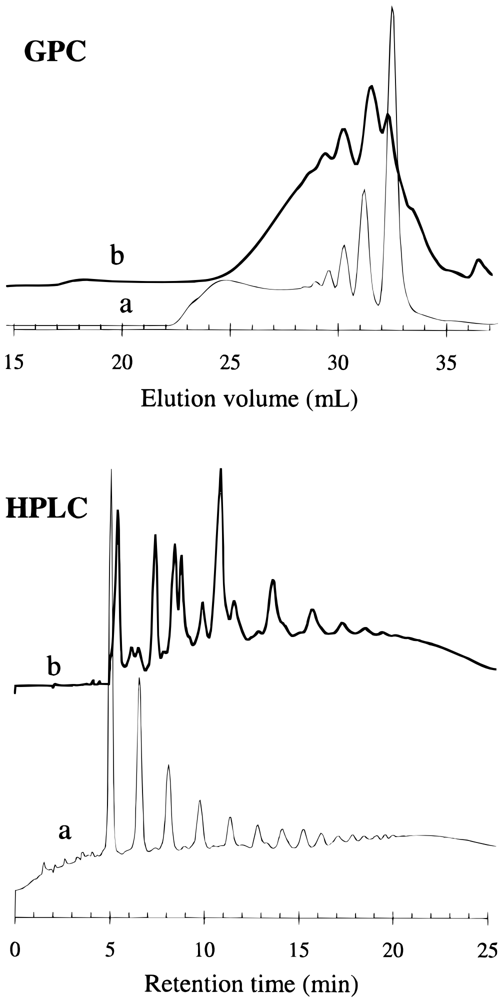
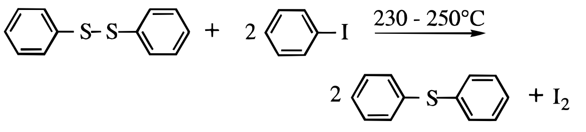


Figure 8. GPC and HPLC trace of (a) macrocyclic oligomers **1** and (b) the reaction mixture of **1** with 2 equiv of 1-iodonaphthalene at 350 °C in *m*-terphenyl under N_2 for 2 h.

Thermolysis of the Macrocyclic Oligomers 1 and the Linear High Molecular Weight Polymer Analog 5 in the Presence of 1-Iodonaphthalene. In a previous publication,[21] we have shown that reaction of diphenyl disulfide with iodobenzene at 230−250 °C resulted in a nearly quantitative conversion of iodobenzene and the formation of diphenyl sulfide and iodine (eq 7). Based on this reaction, a novel synthesis



(7)

of poly(*p*-phenylene sulfide) (PPS) from bis(4-iodophenyl) disulfide was developed.[22] Rule et al. reported[23] that reaction of elemental sulfur with *p*-diiodobenzene at elevated temperatures (230−300 °C) led to formation of PPS prepolymer and extrusion of iodine. The formation of a sulfur radical in this process was also reported.[16] If the ring-opening polymerization of cyclics **1** indeed proceeds via a thiyl radical intermediate, as indicated by the EPR study discussed in the previous section, the polymerization reaction of **1** should be terminated by the addition of an iodo compound. Indeed, we found that heating the cyclic oligomers **1** in the presence of 2 equiv of 1-iodonaphthalaene at 350 °C in *m*-terphenyl under N_2 for 2 h led to the extrusion of iodine. GPC and HPLC analyses (Figure 8) of the resulting material show that the product consisted of

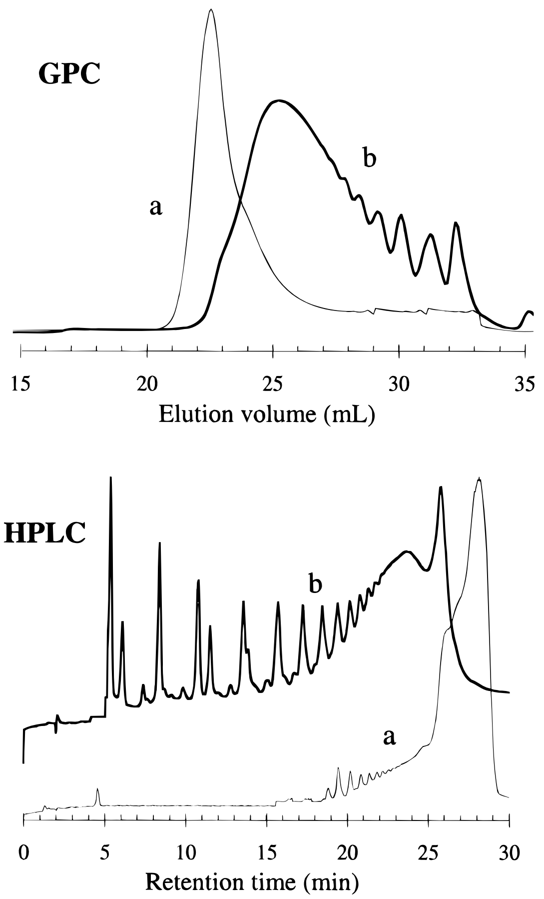


Figure 9. GPC and HPLC trace of (a) high molecular weight linear polymer analog **5** and (b) the reaction mixture of **5** with 2 equiv of 1-iodonaphthalene at 350 °C in *m*-terphenyl under N_2 for 2 h.

low molecular weight oligomers which had $M_n = 1600$ and $M_w = 4000$. Figure 8 clearly shows that the product no longer has the typical pattern of distribution for cyclic oligomers in which the concentration of individual cyclics decreases exponentially as the ring size increases. The reaction of the linear high molecular weight polymer analog **5** with 2 equiv of 1-iodonaphthalene under the same conditions also led to extrusion of iodine and formation of low molecular weight material. GPC and HPLC traces of the polymer analog **5** before and after reacting with 1-iodonaphthalene are shown in Figure 9. The molecular weight of **5** was reduced by a factor of 6 (M_n decreased from 33 800 to 5200, and M_w decreased from 64 800 to 13 000) at the end of the reaction. Gradient HPLC analysis (see Figure 9b) clearly shows the breakdown of high molecular weight polymers and formation of low molecular weight linear oligomers. By analogy with the reaction of elemental sulfur with *p*-diiodobenzene, it may be argued that the formation of thiyl radical is necessary for the reaction of **1** or **5** with 1-iodonaphthalene.

Conclusions

Macrocyclic aryl ether thioether ketone oligomers undergo a facile free-radical transthioetherification reaction both in the melt and in solution to form high molecular weight linear polymers. The presence of thiyl radical(s) during the polymerization reaction was indicated by EPR spectroscopy. The polymerization can be promoted by a catalytic amount of elemental sulfur or an aromatic disulfide DTB and can also be effectively terminated by 1-iodonaphthalene. The molecular weight of the resulting polymers depends on the conversion of cyclics, which suggests that this free-radical ring-opening polymerization has some characteristic features of a step-growth polymerization reaction. The ring-opening polymerization reaction also involves a transthioetherification reaction between linear and cyclic oligomers. The ring−chain equilibrium is much more favorable toward linear polymers. The interchain equilibration is also a facile process during polymerization. This intermolecular transthioetherification has been demonstrated by using a low molecular weight arylene thioether to control the molecular weight of the polymer formed via ring-opening polymerization.

Experimental Section

Materials and General Instruments. Reagent grade solvents and chemicals were used without further purification. 1,2-Bis(4-fluorobenzoyl)-3,6-diphenylbenzene was prepared according to the procedure previously reported.[24] 4,4′-Thiodiphenol, 4-fluorobenzophenone, 1-iodonaphthalene, *m*-terphenyl, elemental sulfur, and 2,2′-dithiobis(benzothiazole) (DTB) were obtained from Aldrich. Macrocyclic aryl ether thioether ketone oligomers **1** were prepared according to the procedure reported previously.[7,14]

^{1}H and ^{13}C NMR spectra were recorded on a Varian Unity-500 NMR spectrometer using $CDCl_3$ as the solvent. Proton spectra were referenced to internal tetramethylsiliane (TMS), while ^{13}C NMR spectra were referenced to the $CDCl_3$ middle line at 77.00 ppm. Matrix-assisted laser desorption/ionization time of flight (MALDI-TOF) mass spectra were recorded on a Kratos Kompact MALDI-III TOF instrument with a maximum laser output of 6 mW at a wavelength of 337 nm (N_2 laser light, 3 ns pulse width, 100 μm diameter spot). The MALDI instrument was operated in a positive reflectron mode. The ions produced from each laser shot were accelerated to 20 keV into a 1 m drift region. An external calibration using bovine insulin and angiotension was used; this provides a mass accuracy within 0.02% for this instrument. The matrix used for the experiment was 1,8,9-anthracenetriol (dithranol) (Aldrich). The sample was prepared by dissolving the cyclic oligomers in 1,1,2,2-tetrachloroethane at a concentration of 5.0 mg/mL. Silver trifluoroacetate (Aldrich) was used as the cationization agent with a stock solution containing 5.0 mg/mL in tetrahydrofuran. A 20 μL portion of the sample solution and 20 μL of the silver trifluoroacetate solution were added to 200 μL of a 10 mg/mL solution of the matrix dissolved in chloroform. This final solution was shaken briefly, and 0.5 μL was applied to a stainless steel sample slide and air-dried prior to analysis.

The GPC analyses of cyclic oligomers and the resulting polymers were carried out on a Waters 510 HPLC using four phenogel 5 μm columns in series (each 300 mm × 7.8 mm i.d., one linear and three 500 Å). Chloroform was used as the eluent with a flow rate of 1.0 mL/min, the UV detector was at 254 nm, and polystyrene standards were used for the calibration. Reversed-phase gradient HPLC analysis was carried out on a Milton Roy CM4000 pump equipped with a reversed-phase column (Primesphere 5 μm C8, 250 mm × 4.6 mm i.d.) and a UV detector at 300 nm; THF/water gradient was used as the eluent at a flow rate of 1.0 mL/min. The gradient program was step 1, 70−85% THF over 25 min at exponent −2; step 2, 85−100% THF over 1 min at exponent 1; step 3, 100% THF for 2 min; and step 4, 100−70% THF over 2 min (recycle).

Synthesis of Thiobis((phenylene-4-oxy)-4-benzoylbenzene) (4). Compound **4** was prepared by an aromatic nucleophilic substitution reaction from the potassium salt of 4,4′-thiodiphenol and 4-fluorobenzophenone. The reaction was conducted in a 100 mL three-neck round-bottom flask equipped with a nitrogen inlet, thermometer, magnetic stirring, Dean−Stark trap, and condenser. The reaction vessel was charged with 4,4′-thiodiphenol (3.307 g, 15.0 mmol), 4-fluorobenzophenone (6.504 g, 31.5 mmol), anhydrous potassium carbonate (4.146 g, 30.0 mmol), *N*,*N*-dimethylacetamide (DMAc) (50 mL), and toluene (10 mL). The resulting mixture was heated under reflux for 2 h, and the temperature was then gradually raised to 165 °C by removing toluene over 30 min. The reaction mixture was kept at 165 °C for 3 h. The reaction mixture was then filtered to remove salts. The filtrate was added to a large excess of vigorously stirred methanol, and the product precipitated as a white solid. Recrystallization of the solid from ethanol gave the desired compound **4**: 8.3 g (95% yield); mp 179 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.04 (d, $J = 2.5$ Hz, 4H), 7.06 (d, $J = 2.9$ Hz, 4H), 7.40 (d, $J = 8.8$ Hz, 4H), 7.48 (t, 4H), 7.58 (t, 2H), 7.77 (d, $J = 7.3$ Hz, 4H), and 7.83 (d, $J = 8.8$ Hz, 4H); MS (EI) m/e 579 (M^+).

Polymerization of the Cyclic Aryl Ether Thioether Ketone Oligomers 1 in the Melt. The melt polymerization of the cyclic oligomers **1** was conducted at 380 °C under N_2 in the presence of a catalytic amount of DTB (0.5−5 mol % based on the repeating unit of the cyclic oligomers). A typical polymerization procedure is illustrated below: cyclic oligomers **1** (2.0000 g, 3.06 mmol based on the repeating unit of the cyclic oligomers) were mechanically mixed with DTB (10.2 mg, 3.06×10^{-2} mmol) in a 50 mL dry test tube. The test tube was sealed with a septum and heated at 380 °C under N_2 for 1 h in a preheated salt bath. The resulting polymer was removed by breaking the test tube. A small portion of the tough material was dissolved into chloroform, and the solution was analyzed by GPC.

Polymerization of the Cyclic Aryl Ether Thioether Ketone Oligomers 1 in Solution. The solution polymerization of cyclic oligomers **1** was conducted at 350 °C under N_2 using *m*-terphenyl as the solvent in the presence of a catalytic amount of elemental sulfur or DTB. A typical procedure is illustrated below: cyclic oligomers **1** (4.0000 g, 6.12 mmol based on the repeating unit of the cyclic oligomers) and elemental sulfur (2.0 mg, 6.12×10^{-2} mmol) were mechanically mixed with *m*-terphenyl (4.0 g) in a 50 mL dry test tube. The test tube was then sealed with a septum and heated at 350 °C under N_2 for 1 h. Upon cooling, the mixture was dissolved into chloroform (50 mL), and the resulting solution was added dropwise into methanol (500 mL) which was vigorously stirred. The polymer precipitated as a fibrous solid, which was filtered and air-dried under house vacuum. The dried polymer was then analyzed by GPC. Solution polymerization of the cyclic oligomers **1** in the presence of the chain transfer agent **4** was also conducted in the same fashion, except that the required amount of the chain transfer agent **4** was added along with the cyclic oligomers.

Thermolysis of the Cyclic Oligomers 1 and Its Linear High Molecular Weight Polymer Analog 5 in the Presence of 1-Iodonaphthalene. (a) Reaction of Cyclic Oligomers 1 with 2 Equiv of 1-Iodonaphthalene. Cyclic oligomers **1** (2.0000 g, 3.06 mmol based on the repeating unit of the cyclic oligomers) and *m*-terphenyl (2.0 g) were mechanically mixed in a 50 mL dry test tube, and then 1-iodonaphthalene (1.5568 g, 6.12 mmol) was added. The test tube was then sealed with a septum and heated at 350 °C under N_2 for 2 h. Upon cooling, the mixture was dissolved into chloroform (30 mL), and the resulting solution was added dropwise into methanol (300 mL) which was vigorously stirred. The product was precipitated as a fine powder, which was filtered and air-dried under house vacuum. The dried powder was then analyzed by GPC and reversed-phase gradient HPLC.

(b) Reaction of Linear High Molecular Weight Polymer 5 with 2 Equiv of 1-Iodonaphthalene. Polymer **5** with $M_n = 33\,800$ and $M_w = 64\,800$ was prepared according to a procedure previously reported.[20] The high molecular weight polymer **5** (1.0000 g, 1.53 mmol based on the repeating unit of the polymer) and *m*-terphenyl (3.0 g) were mechanically mixed in a 50 mL dry test tube, and then 1-iodonaphthalene (0.7775 g, 3.06 mmol) was added. The test tube was then sealed with a septum and heated at 350 °C under N_2 for 2 h. Upon cooling, the mixture was dissolved into chloroform (50 mL), and the resulting solution was added dropwise into methanol (500 mL) which was vigorously stirred. The product was precipitated as a fine powder, which was filtered and air-dried under house vacuum. The dried powder was then analyzed by GPC and reversed-phase gradient HPLC.

Electron Paramagnetic Resonance (EPR) Studies of the Polymerization of the Cyclic Oligomers 1. EPR spectra for the reaction mixtures of the polymerization of cyclic oligomers **1** were 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 polymerization reaction was conducted at 380 °C in an EPR tube which was sealed under high vacuum. After the polymerization, the EPR tube was immediately shock-cooled in liquid nitrogen and stored in liquid nitrogen until analyzed.

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