Synthesis and Ring-Opening Polymerization of Single-Sized Aromatic Macrocycles for Poly(arylene ether)s

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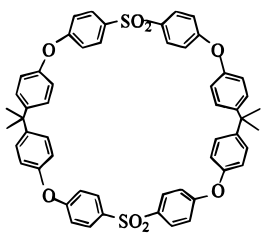
ABSTRACT: Single-sized, pure arylene ether macrocycles (**11**−**21**) ranging from 30 to 60 atom ring sizes were synthesized in good yields (up to 83%) by the two-component method under high dilution conditions. These macrocycles have unsymmetric structures containing sulfone/ketone or sulfone/phosphine oxide functional groups and have relatively low melting points. The melt ROP of the single-sized macrocycles to form poly(arylene ether)s exhibits two-stage characteristics: the first stage is very fast, presumably driven by the large entropy difference between cyclics and linears; the second stage is very slow and is believed to be diffusion controlled due to the high viscosity created in the first stage reaction. The latter stage leads to incomplete polymerization at the low initiator concentrations (1−3 mol %). At high initiator concentrations (5−7 mol %), 100% conversion is reached due to improved initiator distribution in the macrocycles; however, this reduces the molecular weights of the polymers. The molecular weight is found to build up very rapidly, independent of conversion, reaction time, and type of initiator. The ROP is initiated by CsF and alkali phenoxides. The efficiency of the alkali metal counterion is generally in the order $Cs^+ > K^+ > Na^+$, while a phenoxide initiator is more efficient than a fluoride initiator. It is also found that the Cs counterion leads to the highest degree of crosslinking. The ROP of cyclic oligomeric mixtures (**22**) is also reported for comparison; the study shows that the molecular weight depends on time and conversion and that the conversion is sensitive to the content of linear impurities and the average ring size of the cyclic mixtures.

Introduction

Ring-opening polymerization (ROP) plays an important role in production of polymeric materials and has been an active subject of industrial and academic research.[1] A number of commercial polymers, such as nylon-6, poly(ethylene oxide), and poly(dimethylsiloxane), have been prepared by this technique. In recent years, ROP received attention[1c] in production of engineering thermoplastics which typically have very high melt viscosities due to aromatic ring units in the backbones. ROP has the advantage of converting low molecular weight cyclic monomers to high molecular weight polymers without release of volatile byproducts. This allows the use of reactive processing techniques to transform cyclic monomers directly into commercial objects by extrusion or molding. In this manner, the high viscosity problem encountered in processing high molecular weight engineering thermoplastics can be avoided. The technique also opens up the possibility of applications currently not available to high molecular weight engineering thermoplastics due to their high melt viscosities. In particular, ROP would be very useful in fabrication of fiber-reinforced thermoplastic composites since the fiber wetting should be improved with low molecular weight cyclics. Since Bisphenol A based polycarbonate was successfully prepared from the corresponding cyclic oligomeric carbonates,[2] progress has been made in the development and ROP of cyclic monomers for preparation of engineering thermoplastics such as poly(arylene ether)s,[3−13] esters,[14−16] aramides,[17] ether imides,[5−6] and sulfides.[18−20] High molecular weight polymers have been obtained by the ROP in the presence of various initiators, with the ring−chain equilibrium highly favorable toward linear polymers.

In the application of the ROP technique, use of cyclic oligomeric mixtures as monomers is favored commercially because the mixtures have relatively low melting points. One major disadvantage to the use of such complex mixtures, however, is the difficulty of removing low levels of linear oligomers or polymers. The presence of the linear species would influence the rigorousness of fundamental ROP studies and would lead to difficulties in control of the polymerization. Furthermore, individual small ring sized cyclics in the mixture are often highly crystalline with very high melting points despite the fact that the cyclic mixture is initially amorphous with a relatively low softening point. The small cyclics tend to crystallize during the polymerization at reaction temperatures lower than their melting points, thus leading to a mixture of polymer and residual crystalline cyclic impurities.

In order to better understand and control the ROP process in the preparation of engineering thermoplastics, we proposed to use single-sized, pure aromatic macrocycles. The synthesis and ROP of single-sized macrocycles have constituted an undeveloped area. The only example was reported by Colquohoun et al.[4] They synthesized a 35-membered ether ketone macrocycle of high ring strain in moderate yield (40%) for preparation of poly(ether ketone); however, the ROP study was very limited. In our previous papers, we have reported the high yield synthesis of a Bisphenol A based 40-membered ether disulfone macrocycle (**1**).[21] This macrocycle, however, has a very high melting point, above



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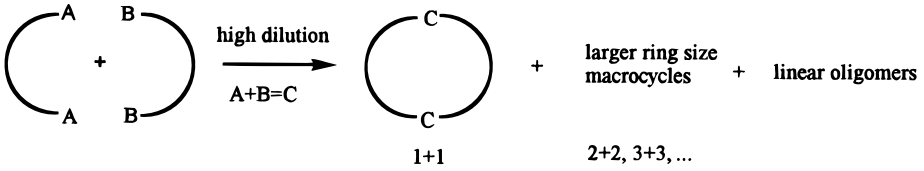
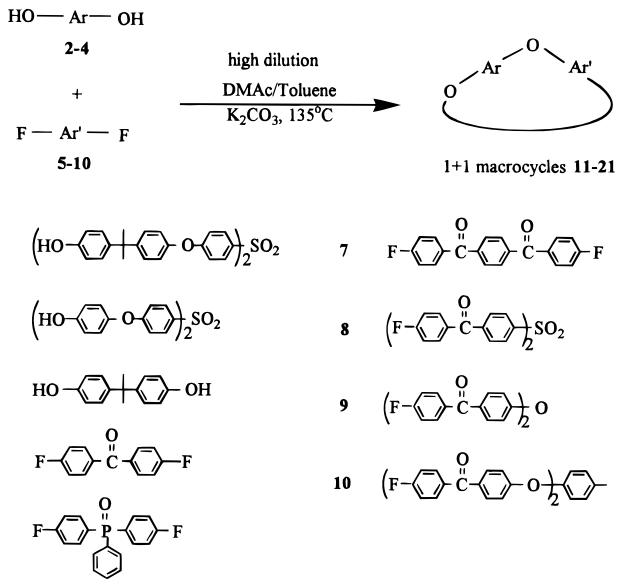
Scheme 1



Scheme 2



500 °C,[21a,22] which precludes its use in ROP directly. To reduce the melting point, unsymmetric arylene ether *co*-macrocycles containing different structural units were prepared and reported herein. As will be shown, the *co*-macrocycles exhibit relatively low melting points, and thus the ROP has been readily investigated. In this paper syntheses and detailed ROP studies of single-sized macrocycles are described. For comparison, we also describe the synthesis and ROP of cyclic oligomeric mixtures.

Results and Discussion

A. Single-Sized Arylene Ether *co*-Macrocycles. The basic principle in the synthesis of macrocycles is the use of high dilution conditions under which the first-order intramolecular cyclization will be favored relative to the second-order intermolecular polycondensation.[23] Our general approach to the synthesis of single-sized macrocycles was through joining two homofunctional components (A−A and B−B) together to form a 1 + 1 macrocycle under high dilution conditions, as shown in Scheme 1. Other larger ring sized macrocycles (2 + 2, 3 + 3, and so on) are also formed, as are linear oligomers and polymers. The formation of the 1 + 1 macrocycle is most favorable, and a high yield can be obtained if the ring strain of this smallest macrocycle is low. Since aromatic macrocycles are rigid, it necessitates that long linear precursors, A−A and/or B−B, be used to release ring strain. By this consideration, long linear precursors **2**, **3** and **8**−**10** (Scheme 2) were thus prepared to meet this requirement. Elongated bisphenol **2** was prepared according to the procedure described in the previous paper in three steps,[21a] while **3** was prepared in 100% yield in one step by reaction of large excess hydroquinone (20 equiv) with bis(4-chlorophenyl) sulfone. Elongated difluoro ketosulfone **8** and ketones **9** and **10** were prepared via Friedel−Crafts reactions according to reported procedures.[24]

Using at least one long precursor in coupling of bisphenols **2**−**4** and difluorides **5**−**10** provided single-sized, 1 + 1 aryl ether *co*-macrocycles **11**−**21** in moderate to excellent yields via aromatic nucleophilic substitution reactions under high dilution conditions (Scheme 2 and Table 1). In the syntheses, the high dilution was achieved by the influx procedure in which both bisphenol and difluoride were dissolved in a small amount of solvent (DMAc) at room temperature, and the solution was then slowly injected via a syringe pump into the reaction flask containing DMAc/toluene and K_2CO_3. The rate of feed v_f[23] ranged from about 3.0×10^{-8} to 1.0×10^{-7} mol/L·s, and the total feed c_f[23] from about 3.0×10^{-3} to 1.6×10^{-2} mol/L. In the cases of difluorides **9** and **10** which are poorly soluble in DMAc at room temperature, the high dilution condition was controlled by addition of small aliquots of the difluoride together with a bisphenol (both dissolved in hot DMAc) in 12 h time intervals. Each feed (the molar amount of each reactant added each time divided by the total amount of solvent used) was 7.7×10^{-4} to 1.3×10^{-3} mol/L, and the total feed was 3.0×10^{-3} to 5.0×10^{-3} mol/L. Both procedures were effective in providing macrocycles in high yields. The detailed structures and yields of the macrocycles are listed in Table 1. It is shown that as high as 83% yield can be obtained by the methods used here. The yields in Table 1 refer to purified macrocycles which were isolated from the crude products by either column chromatography or recrystallization or simply washing with the appropriate solvent. The identity of the macrocycles was confirmed by ^{1}H NMR and FAB-MS. The latter technique provided direct evidence that target macrocycles were obtained.

As also shown in Table 1, these *co*-macrocycles have relatively low melting points, enabling ring-opening polymerization to be readily carried out. Melting points of the ketosulfone macrocycle **11** (366−367 °C) and the sulfone phosphine oxide macrocycle **12** (240, 336 °C) are significantly lower than the corresponding disulfone homomacrocycle **1** (above 500 °C). Generally, the macrocycles containing Bisphenol A moieties (**11**−**18**) have lower melting points than the all-aromatic macrocycles (**19**−**21**). Macrocycles **12** and **15** exhibit two melting transitions by differential scanning calorimetry (DSC), indicating that two crystalline structures can be formed in these macrocycles (polymorphism). TGA data of the macrocycles in Table 1 indicate that these macrocycles have high thermal stability, well above their melting points. Thus, melt ring-opening polymerization at or somewhat above their melting points will not lead to decomposition.

B. Bisphenol A Based Ether Sulfone Cyclooligomeric Mixtures. Cyclooligomeric mixtures **22** were directly synthesized (Scheme 3) from Bisphenol A (BPA) and bis(4-fluorophenyl) sulfone (DFDPS) or bis(4-chlorophenyl) sulfone (DCDPS) following the influx procedure as mentioned above. It was found that cyclic dimer **22** ($n = 2$) (or **1**) was formed in 35% yield in the reaction when DFDPS was used. This macrocycle was previously synthesized in 65% yield[21a] using the two-piece

Table 1. Precursors, Structures, Yields and Physical Properties of Macrocycles

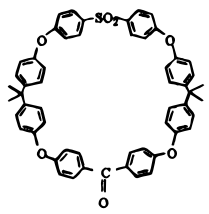
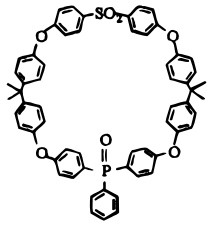
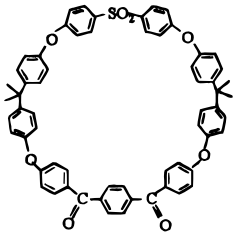
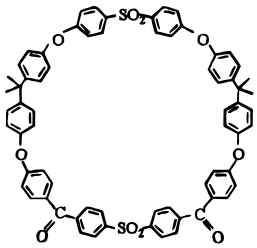
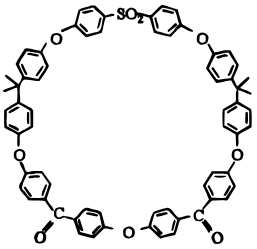
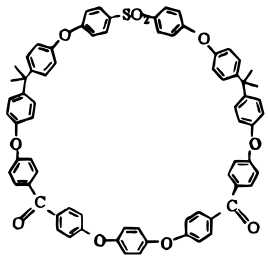
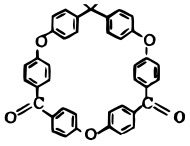
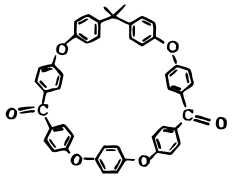
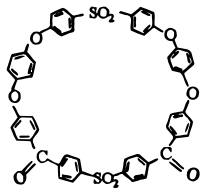
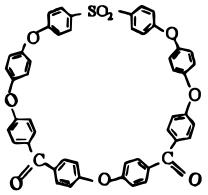
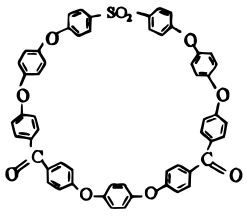
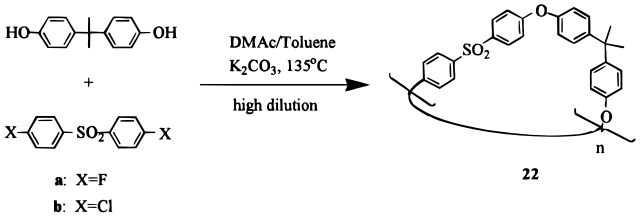
macrocycle	precursors	structure	yield/melting point/TGA (in N_2)
11	**2** + **5**		68% 366.6−367.1 °C 5% wt loss @ 465 °C 30% char @ 800 °C
12	**2** + **6**		44% 240 and 336 °C (DSC) 5% wt loss @ 465 °C 36% char @ 800 °C
13	**2** + **7**		83% 365.9−366.7 °C
14	**2** + **8**		44% 394.8−395.6 °C
15	**2** + **9**		75% 196 and 323 °C (DSC) 5% wt loss @ 483 °C 17% char @ 800 °C
16	**2** + **10**		63% 329.4−331.4 °C 5% wt loss @ 483 °C 48% char @ 800 °C
17	**4** + **9**		66% >400 °C

Table 1 (Continued)

macrocycle	precursors	structure	yield/melting point/TGA (in N_2)
18	**4 + 10**		80% 379.0−381.2 °C 5% wt loss @ 472 °C 52% char @ 800 °C
19	**3 + 8**		21% 407−409 °C
20	**3 + 9**		82% 404.2−406.2 °C
21	**3 + 10**		76% 361.0−363.3 °C 5% wt loss @ 531 °C 54% char @ 800 °C

Scheme 3



combination method by coupling **2** and DFDPS; its melting point is above 500 °C. Removal of the cyclic dimer is necessary, since it quickly crystallizes out of the product mixture upon heating above 300 °C to form a separate crystalline phase inert to melt ring-opening polymerization. The rest of the product is amorphous and completely melts at 300 °C. When DCDPS, a much cheaper reagent, was used, the cyclic dimer was found to contribute 22% in the product mixture. The reduced content of the cyclic dimer was probably due to the lower reactivity of the dichloride, which increased the chance of chain elongation to form larger ring sized macrocycles. Due to lower reactivity of the chlorosulfone, a longer reaction time and a higher dilution condition were required in the synthesis using DCDPS. As analyzed by gel permeation chromatography, the molecular weight of residual products after removal of the dimer is larger for **22b** than that for **22a**. Assuming that these residual products consisted entirely of macrocycles, the average ring size (n) is 5 for **22a** and 8 for **22b**.

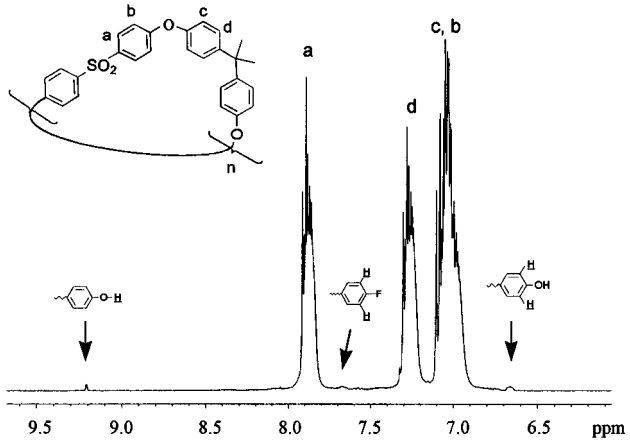


Figure 1. 400 MHz ^{1}H NMR spectrum (aromatic region, in DMSO-d_6) of cyclic mixture **22a**. The arrow marked peaks come from the terminal groups of linear oligomers present in the cyclic mixture.

The residual products of **22a** and **22b** after removal of the cyclic dimer were analyzed by ^{1}H NMR spectroscopy. The presence of terminal groups was detected. As shown in the ^{1}H NMR spectrum (Figure 1) for **22a**, the singlet at 9.2 ppm comes from the terminal phenolic protons, the broad peak at 6.6 ppm from the protons ortho to OH of the terminal phenol, and the broad peak at 7.7 ppm from the protons ortho to F in the terminal halophenyl moieties. On the basis of integral ratios of these small terminal peaks relative to the main peaks

Table 2. Positive Ion MALDI−TOF−MS (in Dithranol Matrix) Data for Cyclic Mixture 22a

signal (*m/e*)	assignment[a]	calculated *m/e*	deviation[c]
906, 944	M_2 + Na, M_2 +Na + K	907, 946	+1, +2
1133	M_3−R[b] + Na	1133	0
1347, 1364	M_3 + Na, M_3 + K	1349, 1365	+2, +1
1789, 1805	M_4 + Na, M_4 + K	1791, 1807	+2, +2
2231, 2247	M_5 + Na, M_5 + K	2234, 2250	+3, +3
2671, 2689	M_6 + Na, M_6 + K	2676, 2692	+5, +3
3115, 3129	M_7 + Na, M_7 + K	3118, 3134	+3, +5
3552	M_8 + Na	3560	+8
3992, 4013	M_9−CH_3 + Na, M_9 + K	3987, 4018	-5, +5
4437, 4452	M_{10} + Na, M_{10} + K	4444, 4460	+7, +8
4867	M_{11}	4863	−4

[a] M_n represents molecular ion with *n* repeating units of structure **22**. [b] R = $C_6H_4SO_2C_6H_4$. [c] Deviation = calculated value − experimental value.

and assuming all the molecules are linear, molecular weights about 10 times higher than those determined by GPC would be predicted. The large discrepancy between the calculated molecular weight and the experimental molecular weight indicates that the samples contain large amounts of macrocycles which have no terminal groups. This is indirect evidence of the cyclic nature of the products although they are contaminated with linears as indicated by the presence of terminal groups. Quantitative estimation of the amount of cyclics present in these products can be made by combining ^{1}H NMR and GPC data, assuming that the linears are terminated by a phenol at the one end and a phenyl halide at the other end. If L is denoted as the integral of the protons ortho to OH of the terminal phenol at 6.6 ppm, and M as the integral of the protons ortho to sulfone at 7.8−8.0 ppm, then the molar percentage of cyclics in the mixtures is $100[(M/4n) - (L/2)]/(M/4n)$, where $L/2$ is proportional to the number of linear molecules present, and $M/4n$ (n is the average number of the repeating units determined by GPC) is proportional to the total number of molecules including cyclics and linears. Assuming that the linears have the same molecular weights as the cyclics, then the molar percentage is equal to the weight percentage. The cyclics in the residual products are thus calculated as follows: **22a**, 79%; **22b**, 84%. If the cyclic dimer is counted, the cyclics in the crude products are 87% and 88%, respectively. It should be pointed out that attempts to remove the linears by solvent extraction were not successful, due to solubility characteristics similar to the cyclics (especially the large macrocycles).

Direct confirmation of the cyclic structures is provided by employing matrix assisted laser desorption/ionization−time of flight−mass spectrometry (MALDI−TOF−MS). By this technique, individual macrocycles in residual products **22a** and **22b** after removal of the cyclic dimer are detected up to $n = 11$ using 1,8,9-anthracenetriol (dithranol) as matrix. Figure 2 gives the MALDI−TOF−MS spectrum for **22a** and Table 2 lists the assignment of each signal in Figure 2 and the corresponding calculated molecular weight. A trace amount of the dimer ($n = 2$) which remains in the product after purification is found in the spectrum. Molecular ions of individual cyclics as well as pseudomolecular ions of the sodium and/or the potassium adducts, where sodium and potassium apparently come from the glass container, are observed. Fragmentation of macrocycles is observed through methyl and ether bond cleavages. No linear oligomers are visible in the spectra. From Table 2, it can be noticed that between the experimental data and the calculated ones there

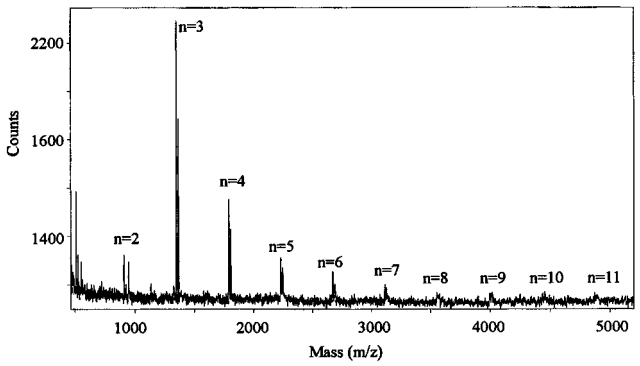


Figure 2. Positive ion MALDI-TOF mass spectrum (in dithranol) of cyclic mixture **22a**.

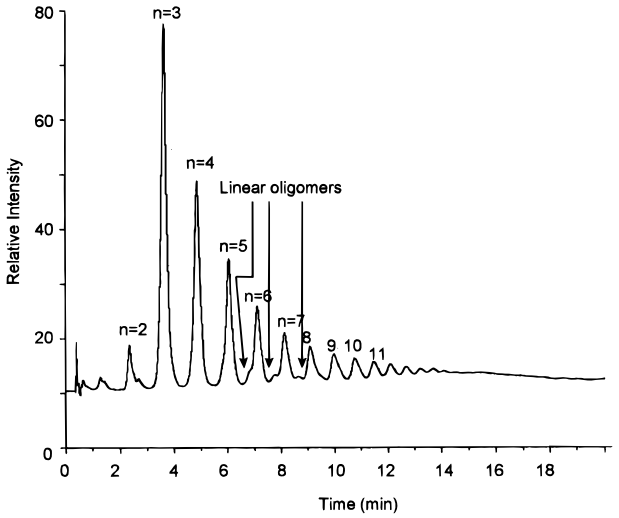


Figure 3. Reverse phase-HPLC chromatogram of cyclic mixture **22a** (C18, THF/water, UV detector at 274 nm).

exist deviations ranging from 1 to 8 mass units. These deviations likely result from low signal to noise ratios of the spectra and calibration error. Addition of $AgCF_3$-CO_2 as a cationization agent in the dithranol matrix reportedly[10] could yield MS spectra of higher quality with better signal to noise ratios.

Reverse phase HPLC with an appropriate choice of solvent combination (THF/water), and gradient program (curved gradient) was found to be a very useful method to achieve a good separation of the individual cyclics of the cyclic mixtures. The HPLC chromatogram for **22a** is shown in Figure 3. It can be seen that the cyclic mixture produced more than eleven peaks which are well separated from each other. The first five eluted peaks correspond to the individual cyclics of ring sizes from $n = 2$ (cyclic dimer) to 6 (cyclic hexamer), since the intensities of these peaks increase once the above macrocycles, which have been obtained in the synthesis of **1** in our previous work,[21a] are added. Linear oligomers are probably located as small shoulders on the cyclic signals.

C. Ring-Opening Polymerization (ROP). The reported ROP studies of arylene ether macrocycles have dealt only with mixtures. As we have indicated above, syntheses of cyclic mixtures inevitably bring in a certain amount of linear oligomers and polymers which are extremely difficult to remove. The presence of these linear species could influence rigorous ROP studies. This should not be a concern when pure macrocycles are used for the ROP. With pure, single-sized arylene ether macrocycles readily available, we herein report the

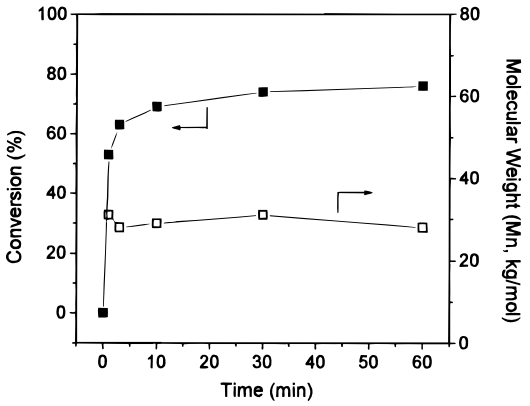


Figure 4. Conversion and molecular weight (M_n) as functions of reaction time in the ROP of macrocycle **12** (1 mol % potassium *p*-phenylphenoxide, at 340 °C under argon).

fundamental studies of ROP of these macrocycles. The ROP studies of cyclic mixtures **22a** and **22b** are also described for comparison.

1. Single-Sized Arylene Ether *co*-Macrocycles. (a) Characteristics of the Polymerization. ROP of single-sized pure macrocycles was most systematically investigated for the 40-membered phosphine oxide sulfone macrocycle **12**. The polymerization of this macrocycle was carried out at 340 °C under argon. Figure 4 shows the conversion and the molecular weight vs time relationships for the polymerization of this macrocycle with 1 mol % of potassium *p*-phenylphenoxide as initiator. Each data point in the figure (as well as in the following figures) corresponds to an individual reaction because it was difficult to remove aliquots from the reaction mixture during the progress of the reaction for analysis. The conversion was determined by proton NMR spectroscopy based on integrals of the peaks corresponding to protons ortho to the sulfone moiety in the macrocycle and in the resultant polymer owing to their different chemical shifts. The molecular weight was determined by gel permeation chromatography (GPC) by universal calibration. From the conversion curve in Figure 4, it is clearly seen that there are two distinct stages in the polymerization. In the first stage (0−3 min), the rate of monomer consumption was very fast, 63% of the macrocycle being consumed within 3 min. The reaction in the second stage (after 3 min) was slow, and only 2% of monomer was consumed during the last 30 min of the reaction. It is also shown that the molecular weight of the polymer was built up rapidly and almost independently of time. The fast buildup of molecular weight suggests that the later stage of the polymerization experiences a highly viscous condition under which diffusion of unreacted macrocycles toward reaction centers was retarded. In fact, during the polymerization, the molten macrocycle thickened rapidly to an unstirrable mass of polymer and unreacted macrocycle. Therefore, the second stage of the polymerization is likely diffusion controlled (the kinetic effect), which is the major reason that leads to incomplete polymerization. The fast reaction in the first stage apparently is driven by a large entropy difference between the macrocycle and the linear polymer. The heat of polymerization may be neglected because the ring sizes are too large to have ring strain although there is no direct experimental evidence to prove that.

Small amounts of gel were formed in the polymerization, as was observed in reported melt ring-opening polymerizations of other aromatic ether macrocycles.[10]

Table 3. Effects of Reaction Time and Alkali Metal Counterion of the *p*-Phenylphenoxide Initiator on the Melt ROP of Macrocycle 12 (1 mol % Alkali Metal *p*-Phenylphenoxide, 340 °C, under Argon)

						conversion (%)	
alkali metal ion	time (min)	M_n (kg/mol)	M_w (kg/mol)	M_w/M_n	gel fraction (%)	by NMR	by GPC
K^+	1.0	31	340	11	0	53	50
	3.0	28	655	24	2	63	63
	10	29	1054	36	2	69	71
	30	31	1160	43	3	74	72
	60	28	1456	52	3	76	73
Cs^+	1.0	21	914	43	0	52	43
	3.0	28	1253	45	3	63	67
	10	26	2029	79	3	67	65
	30	22	2773	128	4	70	72
	60	16	4200	262	8	71	75
Na^+	1.0	26	537	21	0	40	48
	3.0	29	962	34	2	48	50
	10	28	1158	42	8	50	49
	60	23	2679	118	6	63	68

The amount of gel ranged from 0 (1 min) to 3% (60 min) and increased with time (K^+ case, Table 3). The sol fraction of the polymer, extracted by chloroform, was subjected to GPC analyses, which gave tri-modal traces (Figure 5). Peaks at the low retention end of the chromatograms correspond to molecular weights in the millions. These high molecular weight polymers in the sol are due to light crosslinking or branching. The intensities of these peaks increased significantly with time, correlated to higher levels of gel fraction as time increases. Due to branching, molecular weight distributions are anomalously broad. For this particular macrocycle, **12**, a polydispersity index (M_w/M_n) as high as 52 was observed using potassium *p*-phenylphenoxide as initiator (Table 3). Other macrocycles, **11** and **15,** have narrower molecular weight distributions with M_w/M_n below 10 (Table 4). The difference probably relates to the structure of the macrocycles and the mechanism of branching. Further discussion of branching mechanisms is given in Section d.

It is also shown in the GPC traces (Figure 5) that the broad polymer peaks are well separated from the sharp peaks of unreacted starting macrocycle **12**. There are no large ring sized macrocycles observed. The absence of large ring sized macrocycles suggests that depolymerization by the intramolecular ether exchange (illustrated in Scheme 4) did not occur in the polymerization, perhaps due to the fact that the highly viscous conditions created by the initially formed high molecular weight polymer prevent polymer chains from folding.

(b) Effect of Alkali Metal Counterions of Nucleophilic Initiators. The ROP of 40-membered phosphine oxide sulfone macrocycle **12** was also examined using 1 mol % sodium or cesium salt of *p*-phenylphenoxide as initiator. The effect of changing the alkali metal counterion (Na, K, and Cs) on the phenoxide on conversion is shown in Figure 6. It can be seen that the two-stage characteristic of the polymerization is observed with each of these three initiators. As discussed above, the second stage of the polymerization is probably diffusion controlled; thus, the reactivities of the initiators are reflected in the first stage of polymerization (0−3 min). By this consideration, the effect of alkali metal counterion on the reactivity of phenoxide initiator is in the order of Cs = K > Na. Although cesium phenoxide is as reactive as potassium phenoxide, it gives lower conversion overall. In other words, it is less efficient than potassium phenoxide for the ROP of **12**. The

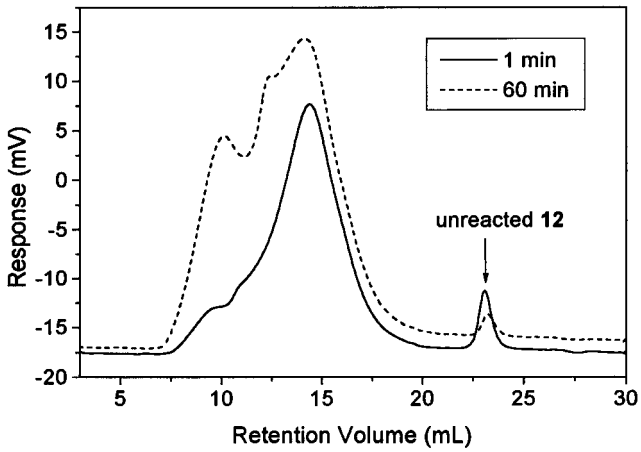


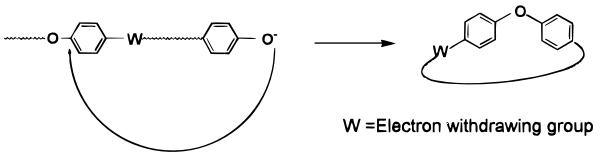
Figure 5. GPC traces ($CHCl_3$, 35 °C, 1 mL/min) of the sol fractions of the ROP products from macrocycle **12** (1 mol % potassium *p*-phenylphenoxide, 340 °C under argon, for 1 and 60 min).

Table 4. Effects of Macrocyclic Structure and Type of Initiator on the Melt ROP under Argon for 30 min (ArOM (M = Na, K, Cs) = Alkali Metal *p*-Phenylphenoxide)

starting cyclic	initiator (mol %)	temp (°C)	M_n (kg/mol)	M_w (kg/mol)	M_w/M_n	gel fraction (%)	conversion (%) by GPC
12	ArONa (1)	340[a]	28	1158	42	8	49
	ArOK (1)	340	31	1160	43	3	72
	ArOCs (1)	340	22	2773	128	4	72
11	ArONa (5)	370	12	42	3.5	10	27
	ArOK (5)	370	13	80	6.4	16	73
	ArOCs (5)	370	11	95	8.6	22	89
15	ArONa (3)	325	35	82	2.3	1	43
	ArOK (3)	325	32	102	3.2	3	75
	ArOCs (3)	325	25	155	6.2	12	97
15	KF (3)	325	52	174	3.4	2	16
	CsF (3)	325	49	224	4.6	19	72

[a] 10 min reaction.

Scheme 4



difference in final conversion for these two initiators obviously comes from the slow second stage of polymerization. Comparing with each other the GPC traces (Figure 7) of the soluble polymers from the polymerizations of **12** using these two initiators, it is seen that the sol fraction from cesium phenoxide contains a significantly higher ratio of polymer with molecular weight above 10^6, indicated by a larger intensity of the peak at about 10 mL retention volume. The higher tendency for branching or crosslinking using cesium phenoxide may have resulted in higher viscosity conditions under which the polymerization was more heavily retarded in the second stage; thus lower conversion was obtained at the end. However, in the polymerization of macrocycles **11** (40-membered ketosulfone) and **15** (50-membered ketosulfone), cesium *p*-phenylphenoxide was found to be more efficient than potassium *p*-phenylphenoxide; higher conversion was obtained with the cesium initiator (Table 4). In these latter two macrocyclic systems, although the cesium counterion also led to a higher degree of branching and crosslinking, the situation might not effectively increase viscosity enough to slow down the polymerization, because these two macrocycles themselves have less tendency for branching (see discussion in section 4) than **12**. Sodium phenoxide is the least reactive initiator, which led to the lowest conversion in the polymerization of all three macrocycles (Tables 3 and 4). It should be pointed out, however, that the rate of molecular weight buildup is nearly independent of whether the polymerization is initiated by sodium, potassium, or cesium phenoxide. In all three initiator systems, the molecular weight (M_n) is built up rapidly and is relatively unchanged during the rest of the polymerization. This can be seen in Table 3.

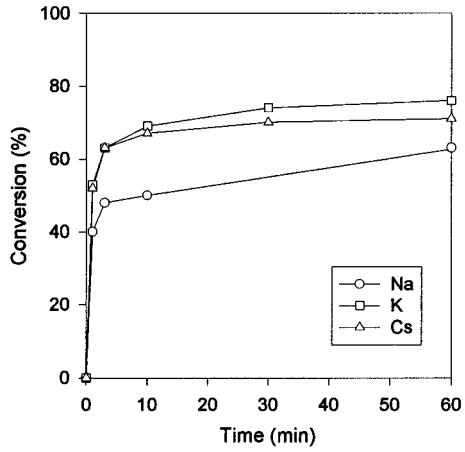


Figure 6. Effect of alkali metal counterion (Na, K, and Cs) on the ROP of macrocycle **12** (1 mol % alkali *p*-phenylphenoxide, at 340 °C under argon).

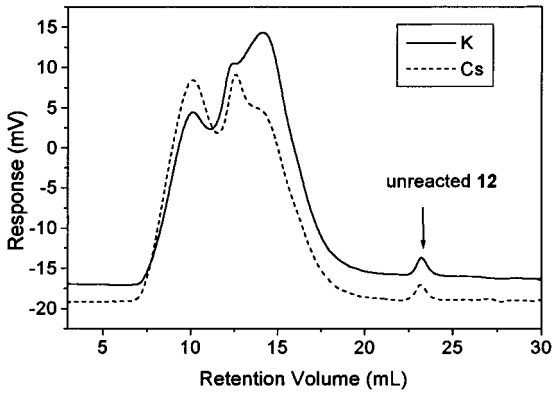


Figure 7. GPC traces ($CHCl_3$, 35 °C, 1 mL/min): the effect of alkali metal counterion on branching in the ROP of macrocycle **12** (1 mol % alkali *p*-phenylphenoxide, 340 °C under argon, for 60 min)

The efficiency of potassium and cesium fluorides as initiators was also examined. Similarly, cesium fluoride is a better initiator than potassium fluoride, though it causes a higher degree of crosslinking. It was found that when the fluorides were used as initiators the conversion was relatively lower than with the phenoxides. For example, cesium fluoride led to 72% conversion in the polymerization of **15**, while cesium *p*-phenylphenoxide led to 97% conversion under the same conditions (Table 4). On the other hand, the molecular weight with cesium fluoride was significantly higher, 49 kg/mol, compared to 25 kg/mol with the cesium phenoxide. The same thing can be found when potassium fluoride and potassium *p*-phenylphenoxide are compared under the same conditions (Table 4). Perhaps the lower conversion using the fluorides as initiators resulted from the higher initial molecular weights which

Table 5. Effect of Temperature on the Melt ROP with Potassium *p*-Phenylphenoxide as Initiator, 30 min Reaction Time

starting cyclic	temp (°C)	M_n (kg/mol)	M_w (kg/mol)	M_w/M_n	gel fraction (%)	conversion (%) by GPC
12[a]	340	31	1160	43	3	72
	355	21	1484	71	6	73
	370	21	1528	72	14	75
15[a]	325	39	144	3.7	2	41
	340	39	159	4.1	6	56
	355	44	203	4.6	5	55
22a[b]	330	20	43	2.2	1	80
	350	31	98	3.1	3	90
	365	25	99	4.0	13	97

[a] 1 mol % initiator, under argon. [b] 0.1 wt % initiator, under vacuum.

led to higher viscosity and thus more restricted motion of polymer chains and unreacted macrocycles during the diffusion-controlled second stage of polymerization. It could also be due to poor fluoride solubility. The different outcomes of the polymerizations using these two types of initiators apparently came from the initiation step in which different nucleophiles were involved in the reaction. After initiation, growing chains in both cases bore phenoxide anion ends which attacked other macrocyclic monomers for chain extension (propagation).

(c) Efforts to Increase Conversion. As we have seen above, the conversion of the polymerization is essentially determined in the first stage of the reaction and further reaction seems to be restricted by the highly viscous condition created by the initially formed high molecular weight polymer. Several experiments were thus carried out to reduce the viscosity of the reaction system, trying to facilitate the second stage of reaction and thereby to increase polymer yields.

(i) Increases of Reaction Temperature. The effect of reaction temperature on conversion was examined for the polymerization of macrocycles **12** and **15** in the presence of 1 mol % potassium *p*-phenylphenoxide under argon for 30 min. It was expected that at higher temperatures polymerization would be more complete, since viscosity should be lower. However, the polymerization of 40-membered phosphine oxide sulfone macrocycle **12** indicates that the conversion was essentially not changed but more polymer was crosslinked when the reaction temperature was increased from 340 to 370 °C (Table 5). The conversion in the polymerization of **15** increased by about 15% when the reaction temperature was increased from 325 to 355 °C (Table 5). Perhaps the effect of reducing viscosity at higher temperatures was offset by an increased viscosity resulting from higher degrees of crosslinking. This is particularly the case in the polymerization of macrocycle **12** since this macrocycle has a higher tendency for crosslinking as reflected by its broader molecular weight distribution and larger gel fractions in its polymerization products. In both cases, molecular weights (M_n) of the sol fractions were relatively unchanged with increases in temperature.

(ii) Increases of the Molar Ratio of Initiator. It is shown in Table 6 that when the molar ratio of initiator, potassium *p*-phenyphenoxide, was increased from 1% to 5% in the polymerization of **12**, the conversion increased from 74% to 100%. The conversions determined by GPC are in good agreement with those determined by NMR. The same general effect was seen in the polymerizations of macrocycles **11** and **15** (Table 6). For macrocycle **15** the conversion increased from 41% to 95%, while for macrocycle **11** the conversion increased from 21% to 81%, as the amount of initiator was increased from 1 to 7 mol %. The increases of conversion with increases of initiator concentration may have resulted from better distribution of the initiator in the macrocycles. For bulk polymerizations, especially the ROP of aromatic macrocycles where the reaction is so fast that molten macrocycles quickly thicken to an unstirrable mass and further reaction is retarded, distribution of the initiator obviously is a critical factor for complete polymerization. Higher concentrations of initiators improved their distribution in the macrocycles and thus gave higher conversions. Another reason for higher conversions when more initiator was used may be reduced viscosity as the result of decreased molecular weight. Lower viscosity could facilitate the diffusion-controlled second stage of the polymerization and thus allow the polymerization to be more complete. Particularly in the polymerizations of macrocycles **12** and **15**, the decrease of molecular weight was relatively large and thus the polymerizations nearly reached completion when potassium *p*-phenylphenoxide was increased to 5 mol %. For the macrocycle **11** since molecular weight decreased slowly, the polymerization was not complete even when the initiator was increased to 7 mol %.

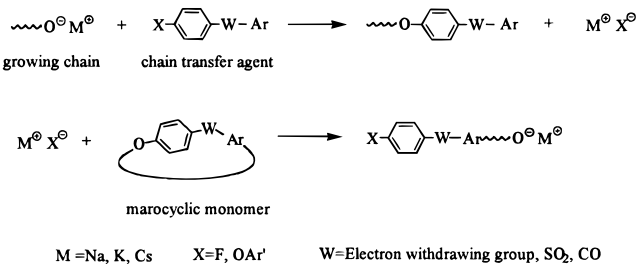
Table 6. Effects of Initiator (Potassium *p*-Phenylphenoxide) Content on the Melt ROP

starting cyclic	initiator content[e]	M_n (kg/mol)	M_w (kg/mol)	M_w/M_n	gel fraction (%)	conversion (%) by NMR	conversion (%) by GPC
11[a]	1.0	20	56	3.0	5	21	19
	1.5	15	66	4.4	6	37	35
	3.0	13	68	5.3	8	59	55
	5.0	13	80	6.4	16	73	70
	7.0	12	77	6.5	25	81	78
12[b]	1.0	31	1160	43	3	74	72
	1.5	25	612	24	3	83	82
	3.0	15	303	19	4	92	94
	5.0	11	242	21	5	100	98
15[c]	1.0	39	144	3.7	2		41
	3.0	32	102	3.2	3		75
	5.0	24	81	3.4	7		94
	7.0	17	58	3.4	5		95
22a[d]	0.1	20	43	2.2	1		80
	0.2	26	69	2.7	1		93
	0.3	28	90	3.3	2		97
	0.5	26	100	3.9	4		98
	1.0	23	104	4.5	14		100

[a] 370 °C, 30 min, under argon. [b] 340 °C, 30 min, under argon. [c] 325 °C, 30 min, under argon. [d] 330 °C, 30 min, under vacuum. [e] mol % for **11**, **12**, and **15**; wt % for **22a.**

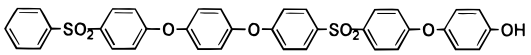
(iii) Addition of Chain Transfer Agents. Chain transfer is a chain-breaking reaction; it results in a decrease in size of the propagating polymer chain. As shown above, when the molecular weight was reduced, higher conversions were obtained. The effect of chain transfer on the polymerization is dependent on whether the reinitiation rate is comparable to that of original propagating species. This means that for our studies the chain transfer reaction must generate a new initiator (M^+X^-), effectively re-initiating the ROP (Scheme 5). In this work, the difluoroketone bis(*p*-fluorobenzoyl)-benzene (**7**) was used as a chain transfer agent, and cesium fluoride and cesium *p*-phenylphenoxide were used as initiators. Thus the new *in situ* generated initiator (M^+X^-) was CsF, which is a relatively good initiator for the ROP as demonstrated above. Unfortunately, addition of the chain transfer agent reduced the conversion instead and 95%−98% of starting mac-

Scheme 5



rocyclic monomers were eventually recovered after reaction when the fluoroketone was increased to 2.5 mol %! The decrease in conversion was also observed by Hay's group when they used an arylene ether sulfone as a chain transfer reagent in the ROP of a cyclic oligomeric mixture.[10] In a model reaction simply using CsF and **7** without addition of the macrocycle, it was found that there were about 5% intractable materials in the product, insoluble even in concentrated sulfuric acid and the soluble part of the product also contained trace amounts of other components besides **7** according to RP-HPLC. Perhaps the reactions between the initiator and the fluoroketone preferentially took place and thus led to destruction of initiation. Due to difficulties in characterization of the intractable material and the trace components in the sol fraction, mechanisms for such reactions could not be elucidated.

(iv) Use of Difunctional Initiator. Hay et al. found that a difunctional initiator was more efficient than a monofunctional initiator in the ROP of a cyclic oligomeric mixture.[10] In our studies using single-sized macrocycles as monomers, a similar situation was observed. It was observed that the dipotassium salt of bisphenol **2** provided a higher conversion (83%) than a monofunctional initiator, the potassium salt of monophenol **23** which provided 64% conversion, in the polymer-



23

ization of macrocycle **12** under the same reaction condition (1 mol % initiator, 340 °C, 30 min under argon). The molecular masses of the polymers in both cases were about the same, in the range of 30 kg/mol. The importance of using difunctional initiators is that high conversions can be more readily achieved without loss of molecular weight. However, because the concentration of phenoxide anions doubled with the difunctional initiator, crosslinking significantly increased, from 2% to 15%.

(d) Model Studies of Cross-Linking. Cross-linking is the common side reaction which takes place in the ring-opening polymerization of aromatic ether macrocycles. Due to the cross-linking, polymerization is not well controlled. Cross-linking also increases viscosity and is believed to be one of the factors limiting conversion of the ROP. Thus, it is important to know what reaction(s) caused cross-linking, in order to be able to better control the ROP. Several model reactions were thus carried out trying to find out the cross-linking mechanism. Although there is no clear answer yet, some clues were obtained.

The reactants used for the model studies were cesium phenoxide and bis(4-phenoxyphenyl) sulfone (**24**). The reaction between these two compounds should yield no new compounds even though ether exchange reactions

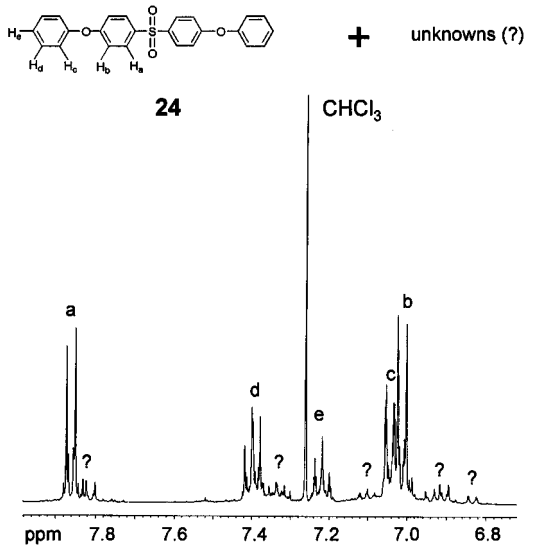


Figure 8. 400 MHz ^{1}H NMR spectrum (in $CDCl_3$) of the crude product from heating a mixture of cesium phenoxide and 4,4′-bis(phenoxyphenyl) sulfone (**24**) at 340 °C for 30 min under argon.

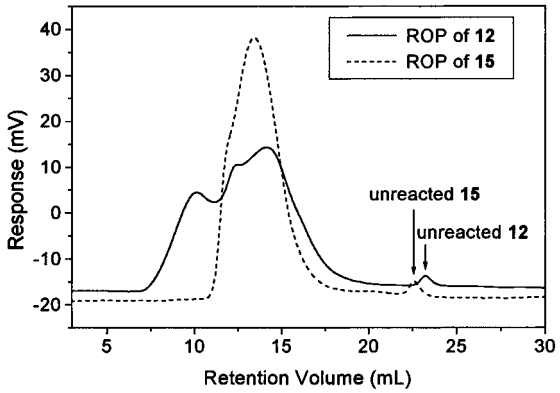


Figure 9. GPC traces ($CHCl_3$, 35 °C, 1 mL/min): the structural effect of macrocycle on molecular weight distribution. ROP of **12:** 1 mol % potassium *p*-phenylphenoxide, 340 °C under argon, for 60 min. ROP of **15**: 1 mol % potassium *p*-phenylphenoxide, 325 °C under argon, for 60 min.

could take place. However, this reaction produced something else. Figure 8 is the ^{1}H NMR spectrum of the product after heating cesium phenoxide and **24** at 340 °C for 30 min under argon. Notice in this NMR spectrum that some small peaks appear within the range of 7.80−7.85 ppm beside the main doublet at 7.86 ppm, which corresponds to the proton ortho to the sulfone group in **24**. These small peaks should come from protons near the sulfone group in the newly generated compound(s). In other words, there was some reaction that occurred on the phenyl ring attached to the sulfone group. Presumably, such a reaction might be the process that led to branched and finally crosslinked polymer in the ROP of aromatic macrocycles containing sulfone (SO_2), ketone (C═O), or phosphine oxide (P═O) functional groups. Some polymerization data may support the above speculation. As pointed out earlier, the polymer from 40-membered phosphine oxide sulfone macrocycle **12** has a much broader molecular weight distribution than the polymers from 40- and 50-membered ketosulfone macrocycles **11** and **15**. In GPC traces (Figure 9), relative to the product for **15**, the polymer from **12** yields a more irregular shaped curve with a large peak at the high molecular weight end of the chromatogram. This may be based on the fact that

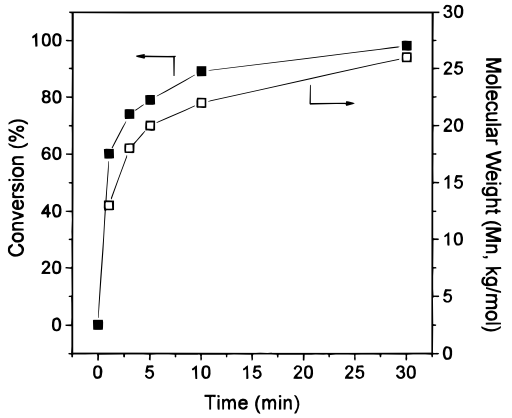


Figure 10. Conversion and molecular weight (M_n) as functions of reaction time in the ROP of cyclic mixture **22a**: 0.5 wt % potassium *p*-phenylphenoxide, at 330 °C under vacuum.

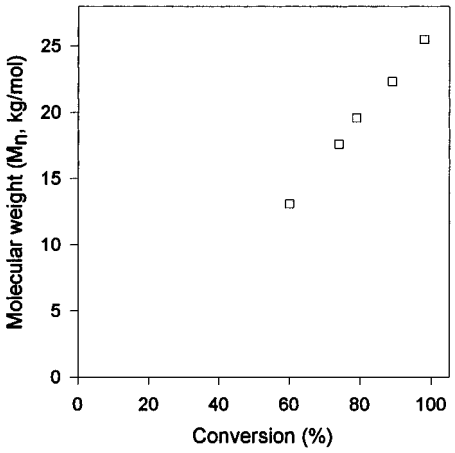


Figure 11. Molecular weight (M_n) as function of conversion in the ROP of cyclic oligomeric mixture **22a** (0.5 wt % potassium *p*-phenylphenoxide, at 330 °C under vacuum).

the phosphine oxide functional group in macrocycle **12** has three phenyl rings attached, providing more potentially reactive sides for branching or crosslinking.

2. Cyclic Mixtures. Similar studies of ring-opening polymerization were carried out with cyclic oligomeric mixtures **22a** and **22b** using potassium *p*-phenylphenoxide as initiator. Since the cyclic dimer ($n = 2$), 24−35% in the mixtures, crystallized out during heating and does not melt below 500 °C, it was removed from the mixtures. The residual cyclic mixture completely melts at about 300 °C, giving a transparent viscous liquid. The polymerization was conducted at 330 °C to make sure that the starting viscosity of the molten cyclic mixture was low.

Figure 10 shows the conversion and the molecular weight vs time relationships for the polymerization of **22a** at 330 °C under vacuum in the presence of 0.5 wt % potassium *p*-phenylphenoxide. Similar to the ROP of single-sized macrocycles, the polymerization shows the same two-stage characteristics: fast in the first stage, but slow in the second stage. However, unlike the polymerization of single-sized pure macrocycles in which high molecular weights were built up rapidly and independently of reaction time, only a medium molecular weight (13K) was obtained initially and then it increased steadily with reaction time and coversion. When the molecular weight is plotted vs conversion, a nearly linear relationship is observed starting from 60% conversion (Figure 11). Since the molecular weight data from the 0% (0 min) to the 60% conversion (1 min) are

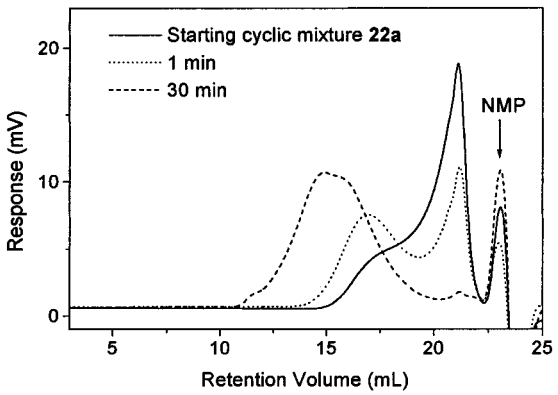


Figure 12. GPC traces (NMP + P_2O_5, 60 °C, 1 mL/min). The ROP of cyclic mixture **22a** in the melt: 0.5 wt % potassium *p*-phenylphenoxide, at 330 °C under vacuum.

not available, the exact relationship between the molecular weight and the conversion in that time span is difficult to know. It should be pointed out that the conversion and the molecular weight of polymer determined by GPC may be overestimated, because the polymer and unreacted cyclic mixture are not well separated and distinguished from each other, especially in the early stage (1 min) of the polymerization (see GPC traces in Figure 12). GPC shows that the polymer peak increases in intensity and moves regularly toward the high molecular weight end of the chromatogram (Figure 12), as time increases. Relatively slow polymerization of the cyclic mixture, compared to the polymerization of above single-sized macrocycles, is due to its large average ring size which lowers the reactivity; this, more or less, lowers the viscosity of the reaction system and thus high conversion is more readily achieved. As normal, gels were also formed and gel content (from 0 to 4%) increased with reaction time (from 1 to 30 min). The molecular weight distribution of the sol polymers increased with time too (from 1.4 to 3.9, M_w/M_n), as more branching took place over the period of the polymerization.

The conversion for the ROP of cyclic mixture **22a** increased with the concentration of initiator, similar to the ROP of single-sized macrocycles. As shown in Table 6, a 100% conversion was achieved in 30 min when the concentration of initiator was increased to 1 wt %. Increasing the concentration of initiator, however, did not sacrifice molecular weights of the resultant polymers. In the range of concentration 0.1−0.3 wt %, the molecular mass actually increased slightly from 20 to 28 kg/mol, whereas the conversion increased from 80 to 97%. The molecular weight slightly decreased with the concentration of initiator starting from 0.3 wt %.

The conversion of **22a** also increased with temperature (Table 5). At 330 °C, only 80% conversion was achieved in the presence of 0.1 wt % potassium *p*-phenylphenoxide, whereas at 365 °C the conversion increased to 97%. The molecular mass (M_n) increased by 11 kg/mol as the temperature was raised from 330 to 350 °C, and then was reduced by 6 kg/mol as the temperature was further raised to 365 °C. Although the polymerization was favorable at 365 °C, crosslinking was more severe. A 13% gel fraction was observed at this temperature, compared to 1% at 330 °C and 3% at 350 °C.

The ROP of the cyclic mixtures **22b** prepared using bis(4-chlorophenyl) sulfone (DCDPS) were not as good as those of **22a** prepared using the corresponding fluoride DFDPS. This cyclic mixture (**22b**) contains

Table 7. Glass Transition Temperatures (T_g's) of the Polymers from ROP

cyclic monomer	Pzn conditions[a]	T_g (°C)[b]
11	6, 5	159
12	3, 3	194
	3, 5	192
	6, 8	188
	6, 9	190
	3, 10	193
15	6, 12	164
22a	6, 16	183
	6, 18	179

[a] Table number, line number. [b] Determined by DSC at 20 °C/min.

about 12% linear oligomers, similar to 13% in **22a**, but its molecular mass, 3.6 kg/mol, is larger than that for **22a**, 2.3 kg/mol. The ROP of **22b** in the presence of 1.0 wt % potassium *p*-phenylphenoxide provided 79% conversion, compared to the 100% conversion in the polymerization of **22a** under the same reaction conditions. This may have resulted from the reaction of the initiator with the chloro-terminated linear oligomers, which generated KCl, which is unable to reinitiate the ROP. We have found that when the amount of linear oligomers containing chlorophenyl sulfone terminal groups increase, the conversion becomes lower. Another possible reason could be its larger ring sizes which resulted in slower reaction because of a smaller entropy force for the ROP. It should be pointed out that in both cases, the ROP needed to be conducted under vacuum conditions; otherwise, the conversions were poorer. This aspect remains for future study.

D. Glass Transitions of the Polymers. The glass transition temperatures (T_g) of the polymers from **11**, **12**, **15** and **22a** analyzed by differential scanning calorimetry are listed in Table 7. For the polymers obtained from the same macrocycle under different conditions, we observed that T_g's are nearly independent of molecular weight and polydispersity. The T_g (183 °C) of Bisphenol A based polyether sulfone obtained by melt ROP of cyclic mixture **22a** is lower than that (195 °C) of the same polymer obtained by solution polycondensation.[28] This difference may be due to branching in the polymer by ROP, since branches prevent entanglement of polymer chains to some extent so that segmental movements of the chains become easier. The new polymers from **11**, **12**, and **15** are 1:1 copolymers of poly(ether sulfone) and a ketone or phosphine oxide unit. The T_g of **11** is close to that (155 °C) of the ketone homopolymer.[29] Similarly the T_g of **15** is close to that (162 °C) of the ketone homopolymer.[29] For **12**, however, the T_g is near both those of the sulfone homopolymer (195 °C)[28] and the phosphine oxide homopolymer (205 °C).[30]

Conclusions

By the two component combination approach, single-sized arylene ether macrocycles ranging from 30 to 60 atom ring sizes were synthesized in moderate to excellent yields through aromatic nucleophilic substitution reactions under high dilution conditions. Due to their unsymmetric structures, these aromatic macrocycles have relatively low melting points. The ROP studies of the single-sized arylene ether macrocycles in the melt revealed several important characteristics of the polymerization. The ROP experiences two stages: the first stage is very fast, presumably driven by the large entropy difference between cyclics and linear polymers; the second stage is very slow and is believed to be diffusion controlled due to the high viscosity resulting from high molecular weight polymers formed in the first stage. Because of the second stage, the polymerization is normally incomplete at low initiator concentrations. Conversion can be increased to 100% by improved distribution of initiator in macrocycles at high initiator concentrations, but at the expense of molecular weight. The molecular weight of the polymers was built up rapidly, independent of conversion, reaction time and type of initiator. The polymerization can be initiated by CsF and alkali phenoxides. In general, an initiator with Cs couterion is more efficient for the ROP than an initiator with K or Na counterion in the order of Cs > K > Na, while a phenoxide initiator is more efficient than a fluoride initiator. Furthermore, a difunctional initiator is more efficient than a monofunctional initiator. Cs is found to be the counterion that causes the highest degree of crosslinking. By comparison, the ROP of cyclic mixtures was relatively slow, and the molecular weight of resultant polymers increased with time and conversion. To some extent, the molecular weight increased with initiator concentration. The polymerization in this case is sensitive to the amount of linear contaminants and the average ring size of macrocycles present in the mixture.

Experimental Section

Measurements. Melting points were taken in capillary tubes with a Melt-Temp II melting point apparatus and have been corrected. Infrared spectra (KBr pellets) were recorded on a Nicolet MX-1 FTIR spectrometer. ^{1}H NMR spectra were obtained on a Varian 400 MHz in deuterated dimethyl sulfoxide or chloroform with TMS as the internal standard at ambient temperature. FAB mass spectra were recorded on a Fisons VG Quattro spectrometer using 3-nitrobenzyl alcohol as matrix. Matrix-assisted laser desorption/ionization time of flight (MALDI−TOF) mass spectra were measured by the Washington University Mass Spectrometry Resource. Reverse-phase HPLC analyses were performed on an ISCO dual pump HPLC system comprising two Model 2350 pumps and the V^4 variable wavelength UV/vis detector set at 274 nm. THF/water curved gradient (curve 6) was used for elution of the products on a reverse-phase column (Novapak 100 Å, 4 μm C18, 150 × 3.9 mm i.d.) at a flow rate of 1.5 mL/min. The gradient program for cyclic mixtures (**22a** and **22b**) was as follows: solvent A, THF/water (65/35) reduced from 100% to 50% over 20 min; at the same time, solvent B, THF increased from 0% to 50% over 20 min. The gradient program for products of ROP of macrocycle **11** was as follows: solvent A, THF/water (60/40) reduced from 100% to 0% over 20 min; at the same time, solvent B, THF increased from 0% to 100% over 20 min. The system was interfaced with the ISCO ChemResearch Chromatographic Data Management/System, used for data analyses. Two sets of gel permeation chromatography (GPC) instruments were used for molecular weight characterization. For cyclic mixtures and polymers obtained from the cyclic mixtures, GPC was carried out in a Waters GPC/ALC 150-C chromatograph equipped with a differential refractometer detector and an on-line differential viscometric detector (Viscotek 150R) coupled in parallel. The mobile phase was NMP containing 0.02 M P_2O_5 and data were recorded at 60 °C at a flow rate of 1.0 mL/min. For polymers obtained from pure macrocycles (**11, 12**, and **15**), GPC was carried out in a Waters 590 chromatograph equipped with a differential refractometer detector (Viscotek Laser Refractometer) and an on-line differential viscometric detector (Viscotek 100) coupled in parallel. The mobile phase was chloroform and data was recorded at 35 °C at a flow rate of 1.0 mL/min. Two columns which were packed with 10^3 and 10^4 Å uStyragel HT were used for both systems. Absolute molecular weights were calculated according to the universal calibration. Thermogravimetric

analyses were performed on a Perkin-Elmer TGA-7 at a scan rate of 10 °C/min in air and N_2 atmospheres. Differential scanning calorimetric analyses were performed on a Perkin-Elmer DSC-7 at a scan rate of 20 °C/min in a N_2 atmosphere; T_g values were taken on second heating scans as the midpoint of the transition.

Linear Precursors 2 and 4−10. Bisphenol A (**4**), bis(4-chlorophenyl) and bis(4-fluorophenyl) sulfone (DCDPS and DFDPS) were purchased from Aldrich and recrystallized in toluene twice prior to use. 4,4′-Difluorobenzophenone (**5**) was purchased from Aldrich and used as received. Monomer grade 1,4-bis(*p*-fluorobenzoyl)benzene (**7**) were supplied by BASF and used as received. Bis[(*p*-((*p*-hydroxyphenyl)isopropylidene)-phenoxy)phenyl] sulfone (**2**) was synthesized by the three-step method given in our previous paper.[21a] Monomer grade bis-(4-fluorophenyl)phenylphosphine oxide (**6**) was prepared according to the reported procedure.[25] Monomer grade bis(4-(*p*-fluorobenzoyl)phenyl) sulfone (**8**) was prepared according to the reported procedure.[24a] Bis[4-(4-fluorobenzoyl)phenyl] ether (**9**) and *p*-bis[4-(4-fluorobenzoyl)phenoxy]benzene (**10**) were synthesized by the method given by Kricheldorf et al.[24b]

Bis[4-(*p*-hydroxyphenoxy)phenyl] Sulfone (3). A mixture of hydroquinone (66.0 g, 600 mmol) and K_2CO_3 (82.9 g, 600 mmol) in DMAc (400 mL) and toluene (250 mL) was refluxed at 133 °C under nitrogen. Water generated from the deprotonation was removed by azeotropic distillation with toluene into a Dean−Stark trap. After 5 h, toluene was distilled, and bis(4-chlorophenyl) sulfone (8.62 g, 30.0 mmol) was added all at once. The reaction was allowed to proceed for 12 h under the nitrogen atmosphere. Upon cooling after reaction, the mixture was neutralized by adding 10% HCl, then precipitated into 2500 mL of water with stirring. The precipitated brown viscous oil was separated, dissolved in 300 mL of chloroform, and washed with distilled water (3 × 100 mL). The organic phase was dried with magnesium sulfate and decolorized with activated carbon. Evaporation of chloroform yielded a pink solid. The solid was dried under vacuum at 80 °C overnight. Yield: 13.0 g (100%). Mp: 196.1−197.9 °C (lit.[26] 187−188 °C); ^{1}H NMR (DMSO-d_6) δ 6.79 (d, 4 H, J = 8.8 Hz), 6.94 (d, 4 H, J = 8.8 Hz), 6.98 (d, 4 H, J = 8.8 Hz), 7.84 (d, 4 H, J = 8.8 Hz), 9.52 (s, 2 H, −OH). FTIR (KBr), cm^{-1}: 3382 (−OH), 3030 (=CH), 1589, 1510, 1490 (C=C), 1231 (C−O−C), 1145 (O=S=O), 832 (aromatic C−H, out of plane).

General Procedure for the Synthesis of Macrocycles 11, 12, 14, 19, 22a, and 22b. The synthesis of **11** is taken as an example. A solution (50 mL) of **2** (10.06 g, 15.00 mmol) and **5** (3.27 g, 15.0 mmol) in DMAc was injected at a rate of 0.8 mL/h into a refuxing suspension of DMAc (600 mL), toluene (300 mL), and K_2CO_3 (3.0 g, 22 mmol). The suspension was mechanically stirred and purged with nitrogen. Water generated was azeotroped by toluene into a Dean−Stark trap. After injection, the reaction was allowed to continue for 24 h. Upon cooling, KF and K_2CO_3 salts were filtered and solvents evaporated; the resultant brown liquid (containing a small amount of DMAc) was then precipitated into water to give an off-white solid. The macrocycle (white solid) was isolated from larger ring size macrocycles and linear oligomers by chromatography using a silica gel column and chloroform/ethyl acetate (50/1) as eluent. Yield: 8.6 g (68%). Mp: 366.6−367.1 °C. A similar procedure was applied for the preparation of **12**, **14**, **19**, **22a**, and **22b**. Yields and melting points of single-sized macrocycles are listed in Table 1.

Cyclo(oxy-1,4-benzoyl-1,4-phenyleneoxy-1,4-phenyleneisopropylidene-1,4-phenyleneoxy-1,4-phenylenesulfonyl-1,4-phenylenoxy-1,4-phenyleneisopropylidene-1,4-phenylene) (11). ^{1}H NMR ($CDCl_3$): δ 1.69 (s, 12 H, $-CH_3$), 6.94 (d, 4 H, J = 8.8 Hz), 6.97 (d, 4 H, J = 8.8 Hz), 6.98 (d, 4 H, J = 8.8 Hz), 7.00 (d, 4 H, J = 8.8 Hz), 7.23 (d, 4 H, J = 8.8 Hz), 7.26 (d, 4 H, J = 8.8 Hz), 7.78 (d, 4 H, J = 8.8 Hz), 7.81 (d, 4 H, J = 8.8 Hz). FABMS: calcd for $C_{55}H_{45}O_7S$, 849.3 [M + H]$^+$ m/z; found, 849.4 [M + H]$^+$ m/z. Anal. Calcd for $C_{55}H_{44}O_7S$: C, 77.81; H, 5.22; S, 3.78. Found: C, 77.86; H, 5.26; S, 3.85.

Cyclo(oxy-1,4-phenylenephenylphosphonyl-1,4-phenyleneoxy-1,4-phenyleneisopropylidene-1,4-phenyleneoxy-1,4-phenylenesulfonyl-1,4-phenyleneoxy-1,4-phenyleneisopropylidene-1,4-phenylene) (12). ^{1}H NMR ($CDCl_3$): δ 1.69 (s, 12 H), 6.95 (d, J = 8.8 Hz, 4 H), 6.96 (d, J = 8.8 Hz, 4 H), 6.97 (d, J = 8.8 Hz, 4 H), 7.00 (d, J = 8.8 Hz, 2 H), 7.01 (d, J = 8.8 Hz, 2 H), 7.21 (d, J = 8.8 Hz, 4 H), 7.25 (d, J = 8.8 Hz, 4 H), 7.38−7.45 (m, 2 H), 7.55−7.53 (m, 1 H), 7.56 (d, J = 8.8 Hz, 2 H), 7.59 (d, J = 8.8 Hz, 2 H), 7.80 (d, J = 8.8 Hz, 4 H). FABMS (in 3-NBA matrix): calcd for $C_{60}H_{50}O_7PS$, 945.3 [M + H]$^+$ m/z; found, 945.3 [M + H]$^+$ m/z. Anal. Calcd for $C_{60}H_{49}O_7PS$: C, 76.25; H, 5.23; S, 3.39. Found: C, 76.15; H, 5.27; S, 3.31.

Cyclo(oxy-1,4-benzoyl-1,4-phenylenesulfonyl-1,4-benzoyl-1,4-phenyleneoxy-1,4-phenyleneisopropylidene-1,4-phenyleneoxy-1,4-phenylenesulfonyl-1,4-phenyleneoxy-1,4-phenyleneisopropylidene-1,4-phenylene) (14). ^{1}H NMR ($CDCl_3$): δ 1.70 (s, 12 H, $-CH_3$), 6.93 (d, 4 H, J = 8.8 Hz), 6.98 (d, 4 H, J = 8.8 Hz), 6.99 (d, 4 H, J = 8.8 Hz), 7.01 (d, 4 H, J = 8.8 Hz), 7.23 (d, 4 H, J = 8.8 Hz), 7.24 (d, 4 H, J = 8.8 Hz), 7.74 (d, 4 H, J = 8.8 Hz), 7.83 (d, 4 H, J = 8.8 Hz), 7.84 (d, 4 H, J = 8.8 Hz), 8.07 (d, 4 H, J = 8.8 Hz). FABMS (in 3-NBA matrix): calcd for $C_{68}H_{53}O_{10}S_2$, 1093 [M + H]$^+$ m/z; found, 1093 [M + H]$^+$ m/z. Anal. Calcd for $C_{68}H_{52}O_{10}S_2$: C, 74.71; H, 4.79; S, 5.86. Found: C, 74.81; H, 4.83; S, 5.75.

Cyclo(oxy-1,4-benzoyl-1,4-phenylenesulfonyl-1,4-benzoyl-1,4-phenyleneoxy-1,4-phenyleneoxy-1,4-phenylenesulfonyl-1,4-phenyleneoxy-1,4-phenylene) (19). The macrocycle was purified by recrystallization in chloroform. ^{1}H NMR ($CDCl_3$): δ 7.01 (d, 4 H, J = 8.8 Hz), 7.04−7.12 (m, 12 H), 7.80 (d, 4 H, J = 8.8 Hz), 7.87 (d, 4 H, J = 8.8 Hz), 7.95 (d, 4 H, J = 8.8 Hz), 8.08 (d, 4 H, J = 8.8 Hz); FABMS (in 3-NBA matrix): calcd for $C_{50}H_{33}O_{10}S_2$, 857.1 [M + H]$^+$ m/z; found, 857 [M + H]$^+$ m/z. Anal. Calcd for $C_{50}H_{32}O_{10}S_2$: C, 70.08; H, 3.76; S, 7.48. Found: C, 70.04; H, 3.76; S, 7.38.

Cyclic Mixtures 22a and 22b. For **22a**, the reaction was allowed to continue for 12 h after the injection, while for **22b** it was 36 h. The reaction mixtures were cooled to room temperature, filtered and rotary evaporated to remove most of the solvent, and then precipitated into water (800 mL, 10 mL of 5% HCl added. The products were boiled in chloroform, and the insoluble dimer (**22**, n = 2) was isolated. Yields of the dimer: 35% (**22a**, n = 2), 24% (**22b**, n = 2). The residual products were further purified by precipitation in methanol. Yields of the residuals: 64% (**22a**), 73% (**22b**), both completely melting at about 300 °C. ^{1}H NMR (DMSO-d_6): d 1.5−1.8 (m, 6nH, −CH_3), 6.9−7.15 (m, 8nH), 7.2−7.35 (m, 4nH), 7.8−8.0 (m, 4nH).

General Procedure for Synthesis of Macrocycles 13, 15, 16, 17, 18, 20, and 21. The synthesis of **13** is taken as an example. To a refluxing suspension of DMAc (400 mL), toluene (220 mL), and K_2CO_3 (0.4 g, 3 mmol) were added four aliquots of **2** (0.3354 g, 0.5000 mmol) and **7** (0.1612 g, 0.5000 mmol) dissolved in hot DMAc (15 mL) at 0, 12, 24, 36 h, respectively. The suspension was mechanically stirred and purged with nitrogen. Water generated was azeotroped by toluene into a Dean−Stark trap. After the fourth addition, the reaction was allowed to continue for 12 h more. Upon cooling, salts were filtered and solvents evaporated; the resultant brown liquid (containing a small amount of DMAc) was then precipitated into water and filtered to give the crude product. Column chromotography (silica gel, 20/1 chloroform/ethyl acetate) was applied to isolate the macrocycle as a white solid. Yield: 1.58 g (83%). Mp: 365.9−366.70 °C. A similar procedure was applied for the preparation of **13**, **15**, **16**, **17**, **18**, **20**, and **21**. Yields and melting points are listed in Table 1.

Cyclo(oxy-1,4-benzoyl-1,4-benzoyl-1,4-phenyleneoxy-1,4-phenyleneisopropylidene-1,4-phenyleneoxy-1,4-phenylenesulfonyl-1,4-phenyleneoxy-1,4-phenyleneisopropylidene-1,4-phenylene) (13). ^{1}H NMR ($CDCl_3$): δ 1.70 (s, 12 H, $-CH_3$), 6.93 (d, J = 8.8 Hz, 4 H), 6.97 (d, J = 8.8 Hz, 4 H), 6.99 (d, J = 8.8 Hz, 4 H), 7.03 (d, J = 8.8 Hz, 4 H), 7.24 (d, J = 8.8 Hz, 4 H), 7.24 (d, J = 8.8 Hz, 4 H), 7.81 (s, 4 H), 7.81 (d, J = 8.8 Hz, 4 H), 7.83 (d, J = 8.8 Hz, 4 H). FABMS (in 3-NBA matrix): Calcd for $C_{62}H_{49}O_8S$, 953.3 [M + H]$^+$ m/z; found, 953.2 [M + H]$^+$ m/z. Anal. Calcd for $C_{62}H_{48}O_8S$: C, 78.13; H, 5.08; S, 3.36. Found: C, 78.19; H, 5.13; S, 3.27.

Cyclo(oxy-1,4-benzoyl-1,4-phenyleneoxy-1,4-benzoyl-1,4-phenyleneoxy-1,4-phenyleneisopropylidene-1,4-phenyleneoxy-1,4-phenylenesulfonyl-1,4-phenyleneoxy-1,4-phenyleneisopropylidene-1,4-phenylene) (15). ^{1}H NMR ($CDCl_3$): δ 1.70 (s, 12 H, $-CH_3$), 6.93 (d, 4 H, J = 8.8 Hz), 6.99 (d, 4 H, J = 8.8 Hz), 7.00 (d, 4 H, J = 8.8 Hz), 7.03 (d, 4 H, J = 8.8 Hz), 7.11 (d, 4 H, J = 8.8 Hz), 7.23 (d, 4 H, J = 8.8 Hz), 7.25 (d, 4 H, J = 8.8 Hz), 7.79 (d, 4 H, J = 8.8 Hz), 7.82 (d, 4 H, J = 8.8 Hz), 7.83 (d, 4 H, J = 8.8 Hz). FABMS (in 3-NBA matrix): Calcd for $C_{68}H_{53}O_9S$, 1045.3 $[M + H]^+$ *m/z*; found, 1045 $[M + H]^+$ *m/z*. Anal. Calcd for $C_{68}H_{52}O_9S$: C, 78.14; H, 5.01; S, 3.07. Found: C, 78.25; H, 5.07; S, 2.96.

Cyclo(oxy-1,4-benzoyl-1,4-phenyleneoxy-1,4-phenyleneoxy-1,4-benzoyl-1,4-phenyleneoxy-1,4-phenyleneisopropylidene-1,4-phenyleneoxy-1,4-phenylene-sulfonyl-1,4-phenyleneoxy-1,4-phenyleneisopropylidene-1,4-phenylene) (16). ^{1}H NMR ($CDCl_3$): δ 1.71 (s, 12 H, $-CH_3$), 6.94 (d, 4 H, J = 8.8 Hz), 6.99−7.03 (m, 16 H), 7.13 (s, 4 H), 7.25 (d, 8 H, J = 8.8 Hz), 7.78 (d, 4 H, J = 8.8 Hz), 7.79 (d, 4 H, J = 8.8 Hz), 7.84 (d, 4 H, J = 8.8 Hz). FABMS (in 3-NBA matrix): calcd for $C_{74}H_{57}O_{10}S$, 1137.4 $[M + H]^+$ *m/z*; found, 1137 $[M + H]^+$ *m/z*. Anal. Calcd for $C_{74}H_{56}O_{10}S$: C, 78.15; H, 4.96; S, 2.82. Found: C, 78.21; H, 5.02; S, 2.74.

Cyclo(oxy-1,4-benzoyl-1,4-phenyleneoxy-1,4-benzoyl-1,4-phenyleneoxy-1,4-phenyleneisopropylidene-1,4-phenylene) (17). ^{1}H NMR ($CDCl_3$): δ 1.73 (s, 6 H, $-CH_3$), 6.97 (d, J = 8.8 Hz, 4 H), 7.01 (d, J = 8.8 Hz, 4 H), 7.02 (d, J = 8.8 Hz, 4 H), 7.32 (d, J = 8.8 Hz, 4 H), 7.66 (d, J = 8.8 Hz, 4 H), 7.67 (d, J = 8.8 Hz, 4 H). FABMS (in 3-NBA matrix): calcd for $C_{41}H_{31}O_5$, 603.2 $[M + H]^+$ *m/z*; found, 603 $[M + H]^+$ *m/z*. Anal. Calcd for $C_{41}H_{30}O_5$: C, 78.70; H, 4.83. Found: C, 78.63; H, 5.00.

Cyclo(oxy-1,4-benzoyl-1,4-phenyleneoxy-1,4-phenyleneoxy-1,4-benzoyl-1,4-phenyleneoxy-1,4-phenyleneisopropylidene-1,4-phenylene) (18). ^{1}H NMR ($CDCl_3$): δ 1.68 (s, 6 H, $-CH_3$), 6.99 (d, J = 8.8 Hz, 4 H), 7.09 (d, J = 8.8 Hz, 4 H), 7.14 (s, 4 H), 7.28 (d, J = 8.8 Hz, 4 H), 7.80 (d, J = 8.8 Hz, 4 H), 7.86 (d, J = 8.8 Hz, 4 H). FABMS (in 3-NBA matrix): calcd for $C_{47}H_{35}O_6$, 695.2 $[M + H]^+$ *m/z*; found, 695 $[M + H]^+$ *m/z*. Anal. Calcd for $C_{47}H_{34}O_6$: C, 81.25; H, 4.93. Found: C, 81.35; H, 4.96.

Cyclo(oxy-1,4-benzoyl-1,4-phenyleneoxy-1,4-benzoyl-1,4-phenyleneoxy-1,4-phenyleneoxy-1,4-phenylenesulfonyl-1,4-phenyleneoxy-1,4-phenylene) (20). ^{1}H NMR ($CDCl_3$): δ 6.97 (d, 4 H, J = 8.8 Hz), 7.02 (d, 4 H, J = 8.8 Hz), 7.08−7.15 (m, 12 H), 7.82 (d, 4 H, J = 8.8 Hz), 7.84 (d, 4 H, J = 8.8 Hz), 7.86 (d, 4 H, J = 8.8 Hz). FABMS (in 3-NBA matrix): calcd for $C_{50}H_{33}O_9S$, 809.1 $[M + H]^+$ *m/z*; found, 809 $[M + H]^+$ *m/z*. Anal. Calcd for $C_{50}H_{32}O_9S$: C, 74.25; H, 3.99; S, 3.96. Found: C, 74.35; H, 4.05; S, 3.84.

Cyclo(oxy-1,4-benzoyl-1,4-phenyleneoxy-1,4-phenyleneoxy-1,4-benzoyl-1,4-phenyleneoxy-1,4-phenyleneoxy-1,4-phenylenesulfonyl-1,4-phenyleneoxy-1,4-phenylene) (21). ^{1}H NMR ($CDCl_3$): δ 6.99−7.08 (m,16 H), 7.11 (s, 4 H), 7.78 (d, 4 H, J = 8.4 Hz), 7.80 (d, 4 H, J = 8.4 Hz), 7.88 (d, 4 H, J = 8.4 Hz). FABMS (in 3-NBA matrix): calcd for $C_{56}H_{37}O_{10}S$, 901.2 $[M + H]^+$ *m/z*; found, 901 $[M + H]^+$ *m/z*. Anal. Calcd for $C_{56}H_{36}O_{10}S$: C, 74.66; H, 4.03; S, 3.56. Found: C, 74.61; H, 4.06; S, 3.49.

Preparation of Initiator Solutions in Ethanol. For preparing CsF and KF ethanol solutions, the two fluorides were directly dissolved in absolute ethanol or ethanol/water. Thus, oven-dried CsF was weighed and dissolved in ethanol to make a 13.13 mM solution in a 1 L volumetric flask. Similarly, oven-dried KF was weighed and dissolved in ethanol with addition of a minimum amount of distilled water to make a 18.30 mM solution in a 250 mL volumetric flask.

For preparing alkali metal (Na, K, or Cs) phenoxide initiators in ethanol, a standardized aqueous alkali hydroxide (NaOH 99.91 mM, KOH 99.41 mM, or CsOH 103.4 mM) solution was placed in a 100 mL flask using a volumetric pipette (4, 10, or 20 mL) and rotary evaporated. The solid hydroxide was then dissolved in ethanol (20 mL). To help dissolve the hydroxide completely, 1−2 mL of distilled water was added. The ethanol solution of the hydroxide was completely transferred into a 200 mL volumetric flask containing an ethanol solution of a phenol which was weighed exactly according to the molar amount of the hydroxide used, and the mixed solution was shaken and diluted to the mark with ethanol. Since phenol **23** has low solubility in ethanol, 5−10 mL of chloroform was added to help dissolve it and 4 mL of standardized aqueous KOH were directly transferred to the phenol solution using a 4 mL volumetric pipette. The specific concentrations of initiator solutions in ethanol are as follows: potassium *p*-phenylphenoxide, 7.993 mM; sodium *p*-phenylphenoxide, 3.976 mM; cesium *p*-phenylphenoxide, 10.34 mM; potassium salt of **2**, 3.996 M; potassium salt of **23**, 1.998 M.

Melt Ring-Opening Polymerization. A dried mixture of a macrocycle and an initiator was first prepared prior to polymerization. For an already finely powdered macrocycle, such as **12** or **15**, a minimum amount of absolute ethanol was added to the cyclic monomer (200.0 mg) placed in a 25 mL round-bottom flask to make a slurry. For macrocycles not finely powdered, such as **11** and **22a**−**22b**, the cyclic monomer (200.0 mg) was dissolved in a minimun amount of chloroform in a 25 mL round-bottom flask, into which a minimum amount of absolute ethanol was then added to precipitate the macrocycle, forming a milky suspension. An ethanol solution of initiator was transferred to the slurry or the suspension using a 1 mL graduated pipette (1/100 scale). To give 5% molar ratio of potassium *p*-phenylphenoxide to macrocycle **12**, for example, 1.32 mL of the salt solution (7.993 mM) was added. Solvents were then carefully rotary evaporated, and the flask was connected to a vacuum line to dry the sample under high vacuum at 110 °C. Once the vacuum reached about 2×10^{-5} Torr over several hours, the sample was purged with argon and re-evacuated three times. For polymerization of single-sized macrocycles, the flask was filled with argon and inserted into a preheated salt bath ($KNO_3/NaNO_2$, 10.0/8.5 by weight). For the polymerization of cyclic mixtures, the evacuated flask was inserted into the preheated salt bath. Time zero was recorded once all the sample melted. After it had cooled to room temperature, the product was immersed in chloroform for 2 h, then removed to a 100 mL beaker, stirred in 50 mL chloroform overnight, and filtered. The filtrate was placed in a pre-weighed flask and rotary evaporated and then dried under vacuum at 100 °C overnight.

4-{*p*-[*p*-(Phenylsulfonyl)phenoxy]phenoxy} 4-(*p*-Hydroxyphenoxy)phenyl Sulfone (23). A mixture of **3** (5.2 g, 12 mmol) and K_2CO_3 (2.0 g, 14 mmol) in DMAc (30 mL) and toluene (15 mL) was refluxed with magnetic stirring for 5 h under nitrogen. Water generated during deprotonation was azeotroped into a Dean−Stark trap by toluene. Toluene was then distilled and 4-chlorophenyl phenyl sulfone (2.53 g, 10.0 mmol) was added all at once. The reaction was allowed to proceed under nitrogen for 12 h at reflux. After it had cooled to room temperature, the reaction mixture was precipitated into dilute HCl (600 mL). The precipitate was filtered, rinsed with water several times, and dried under vacuum. The crude product was then subjected to silica gel column chromatography with chloroform/ethyl acetate (85/15) as eluent, which isolated **23** as a white solid. Yield: 3.56 g (55%). Mp: 215.5−217.0 °C. ^{1}H NMR (DMSO-d_6): δ 6.82 (d, 2 H, J = 8.8 Hz), 6.96 (d, 2 H, J = 8.8 Hz), 7.02 (d, 2 H, J = 8.8 Hz), 7.14 (d, 2 H, J = 9.2 Hz), 7.15 (d, 2 H, J = 9.2 Hz), 7.61−7.71 (m, 3 H), 7.89 (d, 2 H, J = 8.8 Hz), 7.91 (d, 2 H, J = 9.2 Hz), 7.94−7.96 (m, 2 H), 7.96 (d, 2 H, J = 9.2 Hz), 9.53 (s, 1 H). Anal. Calcd for $C_{36}H_{26}S_2O_8$: C, 66.45; H, 4.03; S, 9.85. Found: C, 66.47; H, 4.02; S, 9.91.

Bis(4-phenoxyphenyl) Sulfone (24). A mixture of phenol (6.0 g, 63 mmol) and potassium carbonate (5.0 g, 36 mmol) in *N*,*N*′-dimethylacetamide (40 mL) and toluene (40 mL) was refluxed for 3 h. Water generated was removed in a Dean−Stark trap. Toluene was then distilled and bis(4-chlorophenyl) sulfone (7.18 g, 25.0 mmol) was added. The reaction was allowed to proceed for 12 h. The reaction mixture was poured into water (500 mL) after cooling, and the product was extracted with methylene chloride (3 × 100 mL). The combined organic phase was washed with water, dried with sodium sulfate, and evaporated. Recrystallization in ethanol/chloroform once provided a white solid. Yield: 9.7 g (97%). Mp: 191−193 °C (lit.[27] 141−143 °C). ^{1}H NMR ($CDCl_3$): δ 7.01

(d, 4 H, J = 9.2 Hz), 7.04 (complex d, 4 H, J = 8.8 Hz), 7.22 (complex t, 2 H, J = 8.8 Hz), 7.40 (complex t, 4 H, J = 8.8 Hz), 7.86 (d, 4 H, J = 9.2 Hz).

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References and Notes

(1) (a) Ivin, K. J., Saegusa, T., Eds. *Ring-Opening Polymerization*; Elsevier Applied Science: London, 1984; Vols. 1−3. (b) McGrath, J. E., Ed. *Ring-Opening Polymerization: Kinetics, Mechanisms, and Synthesis*, American Chemical Society: Washington, DC, 1985. (c) Brunelle, D. J., Ed. *Ring-Opening Polymerization/Mechanisms, Catalysis, Structure, Utility*; Hanser Publishers: Munich, Germany, New York, 1993.

(2) (a) Brunelle, D. J. In *Polymeric Materials Encyclopedia*; Salamone, J. C., Ed.; CRC Press: New York, 1996; Vol. 2, p 1677. (b) Brunelle, D. J.; Boden, E. P.; Shannon, T. G. *J. Am. Chem. Soc.* **1990**, *112*, 2399. (c) Brunelle, D. J.; Evans, T. L.; Shannon, T. G.; Boden, E. P.; Stewart, K. R.; Fontana, L. P.; Bonauto, D. K. *Polym. Prepr.* (*Am. Chem. Soc., Div. Polym. Chem.)* **1989**, *30* (2), 569−570. (d) Evans, T. L.; Berman, C. B.; Carpenter, J. C.; Choi, D. Y.; Williams, D. A. *Polym. Prepr.* (*Am. Chem. Soc., Div. Polym. Chem.)* **1989**, *30* (2), 573. (e) Stewart, K. R. *Polym. Prepr.* (*Am. Chem. Soc., Div. Polym. Chem.)* **1989**, *30* (2), 575.

(3) (a) Mullins, M. J.; Woo. E. P.; Murray, D. J.; Bishop, M. T. *CHEMTECH*, **1993** August, 25. (b) Mullins, M. J.; Woo, E. P.; Chen, C. C.; Murray, D. J.; Bishop, M. T.; Balon, K. E. *Polym. Prepr.* (*Am. Chem. Soc., Div. Polym. Chem.)* **1991**, *32* (2), 174. (c) Mullins, M. J.; Galvan, R.; Bishop, M. T.; Woo, E. P.; Gorman, D. B.; Chamberlin, T. A. *Polym. Prepr.* (*Am. Chem. Soc., Div. Polym. Chem.)* **1992**, *33* (1), 414. (d) Mullins, M. J.; Woo, E. P. U.S. Patent 5,264,520 to Dow Chemical, 1993. Mullins, M. J.; Woo, E. P.; Balon, K. E.; Murray, D. J.; Chen, C. C. U.S. Patent 5,264,538 to Dow Chemical, 1993.

(4) Colquohoun, H. M.; Dudman, C. C.; Thomas, M.; Mahoney, C. A.; Williams, D. J. *J. Chem. Soc., Chem. Commun*, **1990,** 336.

(5) Cella, J. A.; Talley, J. J.; Fukuyama, J. M. *Polym. Prepr.* (*Am. Chem. Soc., Div. Polym. Chem.)* **1989**, *30* (2), 581.

(6) Cella, J. A.; Fukuyama, J.; Guggenheim, T. L. *Polym. Prepr.* (*Am. Chem. Soc., Div. Polym. Chem.)* **1989**, *30* (2), 142.

(7) (a) Chan, K. P.; Wang, Y.; Hay, A. S. *Macromolecules* **1995,** *28*, 653. (b) Chan, K. P.; Wang, Y.; Hay, A. S.; Hronowski, X. L.; Cotter, R. J. *Macromolecules* **1995**, *28*, 6705−6717. (c) Ding, Y.; Hay, A. S. *Macromolecules* **1996**, *29*, 3090−3095.

(8) Wang, Y,; Chan, K. P.; Hay, A. S. *J. Appl. Polym. Sci.* **1996**, *59*, 831−843.

(9) Wang, Y,; Chan, K. P.; Hay, A. S. *Macromolecules* **1996**, *29*, 3717−3726.

(10) Wang, Y.; Chan, K. P.; Hay, A. S. *J. Polym. Sci., Part A: Polym. Chem.* **1996**, *34*, 375−385.

(11) Gao, C.; Hay, A. S. *Polymer* **1995**, *36*, 4141−4146.

(12) Wang, Y.; Paventi, M.; Hay, A. S. *Am. Chem. Soc. Div. Polym. Chem. Polym. Prepr.* **1995**, *36* (2), 128−129.

(13) Wang, Y.; Paventi, M.; Chan, K. P.; Hay, A. S. *J. Polym. Sci., Part A: Polym. Chem.* **1996**, *34*, 2135−2148.

(14) Guggenheim, T. L.; McCormick, S. J.; Kelly, J., J.; Brunelle, D. J. ; Colley, A. M.; Boden, E. P.; Shannon, T. G. *Polym. Prepr.* (*Am. Chem. Soc., Div. Polym. Chem.)* **1989**, *30* (2), 579.

(15) Gibson, H. W.; Ganguly, S.; Yamaguchi, N.; Xie, D.; Chen, M.; Bheda, M.; Miller, P. *Polym. Prepr.* (*Am. Chem. Soc., Div. Polym. Chem.)* **1993**, *34* (1), 576−577.

(16) (a) Hubbard P.; Brittain, W. J. *Polym. Prepr.* (*Am. Chem. Soc., Div. Polym. Chem.)* **1995**, *36* (2), 136−137. (b) Hubbard P.; Brittain, W. J. *Polym. Prepr.* (*Am. Chem. Soc., Div. Polym. Chem.)* **1996**, *37* (1), 238−239. (c) Hubbard P.; Brittain, W. J.; Simonsick, W. J., Jr.; Ross, C. W., III. *Macromolecules* **1996**, *29*, 8304.

(17) (a) Guggenheim, T. L.; McCormick, S. J.; Guiles, J. W.; Colley, A. M. *Polym. Prepr.* (*Am. Chem. Soc., Div. Polym. Chem.)* **1989**, *30* (2), 138. (b) Memeger, W. Jr.; Lazar, J.; Ovenall, D.; Arduengo, A. J., III; Leach, R. A. *Macromol. Symp.* **1994**, *77*, 105−116. C) Kim, Y. H.; Calabrese, J.; McEwen, C. *J. Am. Chem. Soc.* **1996**, *118*, 1545. (c) Memeger, W., Jr., In *Polymeric Materials Encyclopedia*; Salamone, J. C., Ed. CRC Press: New York, 1996; Vol. 6, p 3873.

(18) Wang, Y.; Hay, A. S. *Macromolecules* **1996**, *29*, 5050−5053.

(19) Wang, Y.-F.; Chan, K. P.; Hay, A. S. *Macromolecules* **1995,** *28*, 6371.

(20) Ding, Y.; Hay, A. S. *Macromolecules* **1996**, *29*, 4811−4812.

(21) (a) Xie, D.; Gibson, H. W. *Macromol. Chem. Phys.* **1996**, *197*, 2133−2148. (b) Ganguly, S.; Gibson, H. W. *Macromolecules*, **1993,** *26*, 2408.

(22) Colquhoun, H. M.; Williams, D. J. *Macromolecules*, **1996**, *29*, 3311.

(23) (a) Knops, P.; Sendhoff, N.; Mekelburger, H. B.; Vögtle, F. *Top. Curr. Chem.* **1991**, *161*, 1. (b) Rossa, L.; Vogtle, F. *Top. Curr. Chem.* **1983**, *113*, 1.

(24) (a) Staniland, P. A.; Wilde, C. J.; Bottino, F. A.; Pasquale,G. D.; Pollicino, A.; Recca, A. *Polymer* **1992**, *33*, 1977. (b) Kricheldorf, H. R.; Delius, U.; Tonnes, K. U. *New Polym. Mater.* **1988**, *11*, 127.

(25) (a) Smith, C. D.; Gungor, A.; Keister, K. M.; Marand, H. A.; McGrath, J. E. *Polym. Prepr.* (*Am. Chem. Soc., Div. Polym. Chem.)* **1991**, *32* (1), 95. (b) Hirose, S.; Nakamura, K.; Hatakeyama, T.; Hatakeyama, H. *Sen-I Gakkaishi*, **1987**, *43* (11), 595.

(26) Bayer, A. G. Patent: FR 1,514,802, 1966; *Chem. Abstr.* **1969**, *70*, 87309z.

(27) Amiri, M. *J. Chem. Soc., Perkin Trans. 2* **1979**, *8*, 7.

(28) Johnson, R. N.; Farnham, A. G.; Clendinning, R. A.; Hale, W. F.; Merriam, C. N. *J. Polym. Sci., Part A-1* **1967**, *5*, 2375.

(29) Hergenrother, P. M.; Jensen, B. J.; Havens, S. J. *Polymer* **1988**, *29*, 358.

(30) Smith, C. D.; Grubbs, H.; Webster, H. F.; Gungor, A.; Wightman, J. P.; McGrath, J. E. *High Perform. Polym.* **1991**, *3*, 211.

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