Synthesis and Characterization of Novel Cyclic (Aryl Ether Ketone)s, Cyclic (Aryl Ether Phthalazine)s, and Cyclic (Aryl Ether Isoquinoline)s

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ABSTRACT: The efficient preparation of a range of cyclic (aryl ether ketone)s containing the 1,2-dibenzoylbenzene moiety via the nucleophilic aromatic substitution route with the use of the pseudo-high dilution principle was developed. Chemical transformation of the 1,2-dibenzoylbenzene moiety of these cyclic (aryl ether ketone)s led to the preparation of novel cyclic (aryl ether phthalazine)s and cyclic (aryl ether isoquinoline)s. The preparation of cyclic (aryl ether ketone)s from 4,4′-difluorobenzophenone and 1,3-bis(4-fluorobenzoyl)benzene is also discussed. Detailed structural characterization of these novel oligomers by matrix-assisted laser desorption ionization time-of-flight mass spectrometry (MALDI-TOF-MS), ^{13}C and ^{1}H NMR, GPC, and HPLC confirmed the cyclic nature and revealed the composition of the oligomeric mixtures prepared. MALDI-TOF-MS, which enables the detection of oligomers with mass up to 5000 Da, was shown to be a very powerful tool for the analysis and proof of the cyclic nature of the oligomers. Thermoanalyses show that most of these oligomers exhibit a high degree of crystallinity while their corresponding polymers are amorphous.

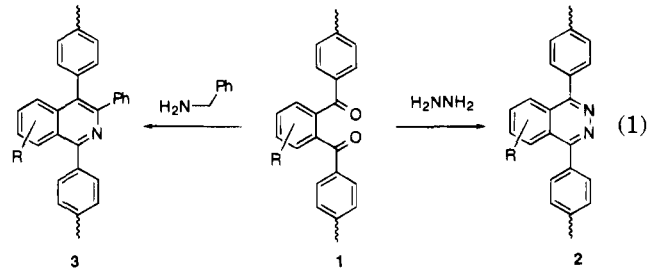
1. Introduction

Poly(aryl ether)s are high-performance polymers which have excellent mechanical strength per unit weight, high thermal stability, chemical resistance, and good insulating properties. Many high-performance polymers are very difficult to process due to their high softening temperature and high melt viscosity. The development of readily processible precursors of high-performance polymers would undoubtedly broaden the future applications of these excellent materials.[1]

In recent years, the advantages of using cyclic oligomers as precursors of thermoplastics has been well recognized.[2,3] The cyclic oligomers offer a unique combination of low melt viscosity and the possibility of undergoing controlled polymerization in the melt without the liberation of volatile byproducts. We are particularly interested in exploring the feasibility of utilizing cyclic oligomers of poly(aryl ether)s as reactive intermediates. In the area of cyclic (aryl ether)s, pioneering work has been reported by scientists from Imperial Chemical Industries, General Electric Co., and Dow Chemical Co.[3]

However, up to now, no general convenient and high-yield synthesis for cyclic (aryl ether)s has been available. Hence, the studies of polymerization and physical properties are rather scarce in the literature. Therefore, one of our objectives was to develop a better synthesis for cyclic (aryl ether) oligomers.

Recently, we reported an efficient synthesis of cyclic (aryl ether) oligomers which proceeds in high yield. Preliminary studies indicate that these oligomers undergo melt polymerization readily in the presence of anionic catalysts.[4] These cyclic oligomers contain a 1,2-dibenzoylbenzene moiety **1**[5] which can be quantitatively transformed to a phthalazine **2**[6] or isoquinoline **3**[7] (eq 1). Hence, we have a very easy way to obtain cyclic



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phthalazines and isoquinolines which would otherwise be difficult to obtain. In addition, as we have reported previously, poly(aryl ether ketone)s that contain the 1,2-dibenzoylbenzene moiety and the corresponding poly(aryl ether phthalazine)s and poly(aryl ether isoquinoline)s are high-performance polymers which exhibit excellent thermal stability and mechanical properties.[5-7] Hence, these cyclic oligomers should be attractive candidates as reactive intermediates for the synthesis of high-performance polymers.

Herein, we will discuss our further studies in synthesis and characterization of these cyclic (aryl ether ketone), (aryl ether phthalazine), and (aryl ether isoquinoline) oligomers.

2. Results and Discussion

2.1. Synthesis of Cyclic (Aryl Ether Ketone) Oligomers Containing the 1,2-Dibenzoylbenzene Moiety. Cyclic (aryl ether ketone)s containing a 1,2-dibenzoylbenzene moiety were prepared by the aromatic nucleophilic substitution route utilizing an AA + BB approach, in which difluoro monomers **4**, **5**, and **6** were allowed to condense with bisphenols **7** to give the corresponding cyclic oligomers **8**, **9**, and **10** (Scheme 1 and Table 1). The difluoro monomers **4**, **5**, and **6** were prepared according to the reported method.[5]

Pseudo-High Dilution Principle. The synthesis of cyclic oligomers is not trivial, especially if one would like to prepare these materials conveniently in high

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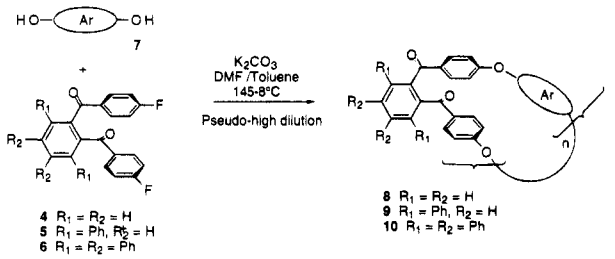
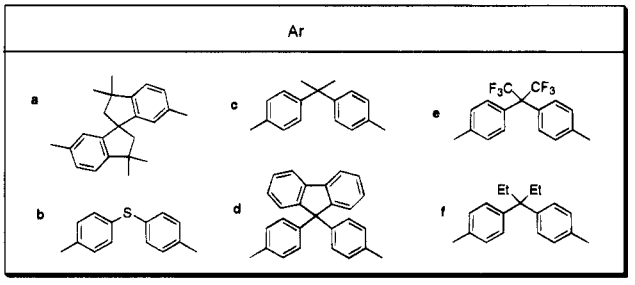
Table 1. Yields and Physical Properties of Cyclic Oligomers

cyclic oligomer	m:n	yield[a] (%)	M_w[b] (kg/mol)	M_n[b] (kg/mol)	T_g[c] (°C)	T_m[c] (°C)	TGA[d] (°C)
8a		80	2.1	1	186 (197)	350	481
8b		90	3.1	1.3	142 (156)	234	476
8c		95	4.8	1.5	157 (180)	324	452
8d		80	5.1	1.7	220 (240)	nd	517
9b		90	5.7	1.9	189 (198)	388	462
9c		80	5.3	1.9	194 (221)	>450	480
9d		80	10.3	2	254	nd	479
9e		95	5.8	1.7	200	365	526
9f		70	5.4	1.5	177	412	483
10b		36	11.6	1.8	218	395	452
22		80	11.4	0.5	222 (234)	415	450
14b	1:1	85	4.8	1.5	169	nd	455
15b	3:1	85	4	1.3	180	nd	475
16c	1:1	85	5.4	1.4	180	nd	473
17b	1:1	85	8.5	1.5	195	nd	450
18d	1:1	95	6.2	1.7	219	nd	461
19e	1:1	95	6.8	1.7	201	354	528
23a		90			230 (250)	nd	420
23b		90			nd	nd	480
23c		80			217 (215)	nd	450
24c		85			211 (226)	nd	530
28b		0.9	0.8	130	496	274/364	80
28c		5.9	1.3	160	500	355	88
30b		12.6	2.2	141	486	284	78

[a] Isolated yield. [b] Measured by GPC and calibrated against polystyrene standards. [c] Measured by DSC under a nitrogen atmosphere (50 mL/min); the heating rate was 20 °C/min. The number in parentheses is the T_g of the corresponding high molecular weight linear polymer. [d] Reported 5% weight loss under a nitrogen atmosphere (200 mL/min); the heating rate was 20 °C/min. [e] nd = not detected.

Scheme 1





purity and high yield. Synthesis of cyclic oligomers is very often complicated by the formation of linear oligomers and high molecular weight polymer via the competing polycondensation reactions.

Selective formation of cyclic oligomers can be achieved by the use of dilute conditions which favor cyclization and suppress polycondensation, since cyclization is a first-order reaction and polycondensation is a second-order reaction. However, using a large volume of solvent would not be a viable approach. In order to achieve a practical synthesis of cyclic oligomers, a pseudo-high dilution principle[8] was employed. Instead of using a large amount of solvent, a pseudo-high dilution condition can be created by slow addition of the reactants into the reaction vessel at such a rate that a steady low concentration of unreacted end groups is maintained, hence favoring the formation of cyclic oligomers even with a very high product concentration buildup.

One critical factor in applying the pseudo-high dilution principle is the rate of addition of reactants, which is very much dependent on the rate of reaction. A general rule of thumb is that the higher the rate of reaction, the faster the rate of addition can be employed. We therefore used fluoro monomers instead of their chloro analogs because an aryl fluoride activated by a carbonyl or sulfone group in the *ortho* or *para* position is at least 100 times more reactive than an aryl chloride in aromatic nucleophilic substitution with phenoxide,[9] so that shorter addition times can be employed.

Thus, a concentrated *N,N*-dimethylformamide (DMF) solution of reactants (0.6 M) is pumped into the reaction vessel containing solvent (DMF) and base (K_2CO_3) over a period of 8 h. The final concentration of the product can be as high as 40 mM. Toluene is used for continuous azeotropic removal of water generated during the reaction. The amount of toluene used is kept minimal, because its presence reduces the polarity of the solvent system and hence slows down the reaction rate. Following the addition of reactants, it takes another 8 h of reflux to ensure complete reaction.

When the final solution concentration is doubled to 80 mM, with the rate of addition unchanged, the high molecular weight fraction increases at the expense of the yield of cyclic oligomers. Gel permeation chromatographic (GPC) traces of cyclic oligomers **9c** obtained at two different concentrations illustrate this point (Figure 1i). We generally employ K_2CO_3 as base; however, we found that using Cs_2CO_3 as base reduced the reaction time by half, from a total of 16 to 8 h. Cesium phenoxide has been shown to have a higher reactivity than potassium phenoxide in these displacement reactions.[10]

Formation of Cyclic Oligomers 8a from Spirobiindanediol (SBI) 7a. When bisphenol **7a** was used as the bisphenol to prepare cyclic oligomers **8a**, a high yield of cyclic materials was obtained without the use of the pseudo-high dilution condition as described above. A batch process was used and the concentration of the reaction mixture can be as high as 100 mM with a reaction time of 8 h. This can be explained in terms of

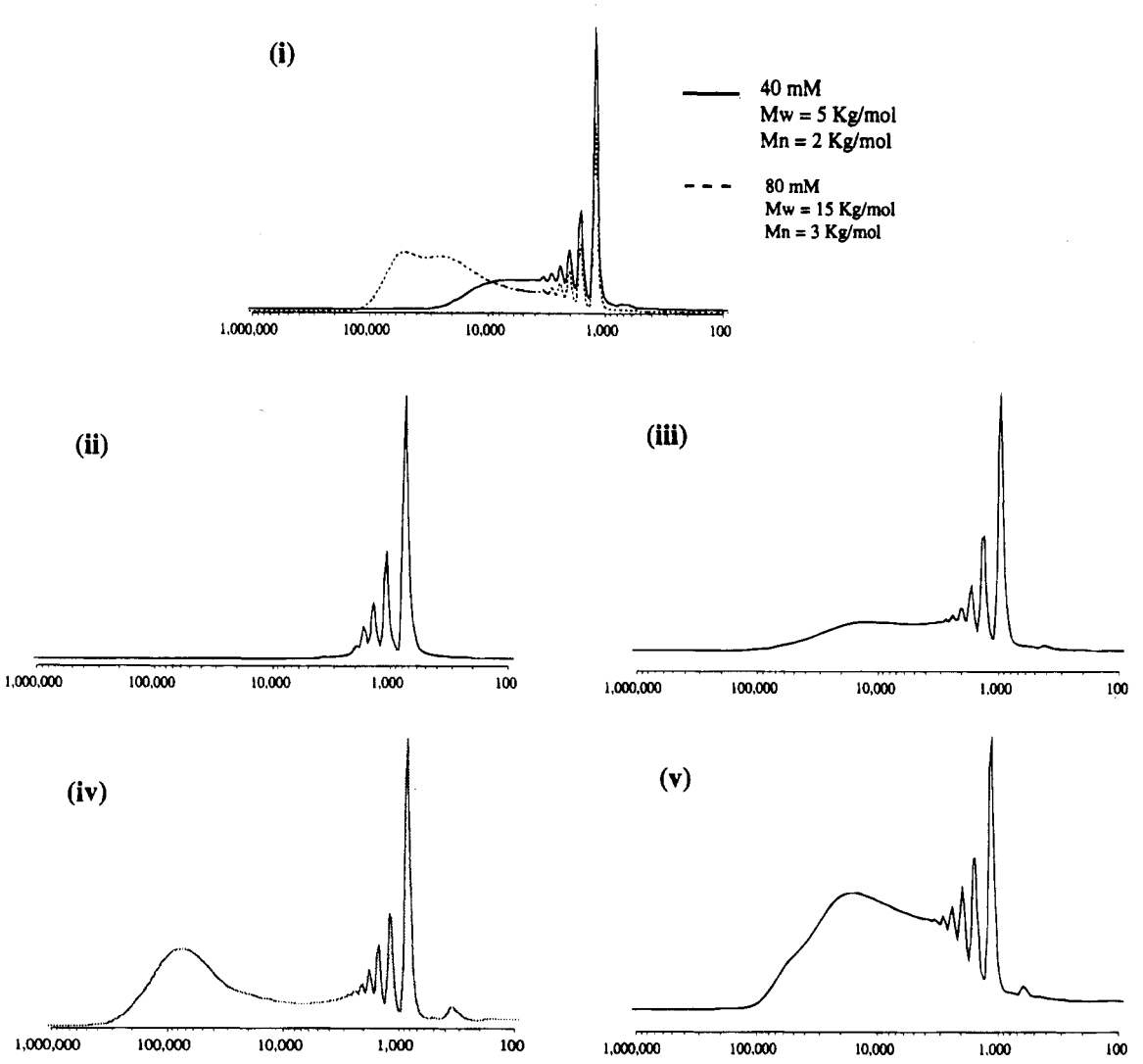
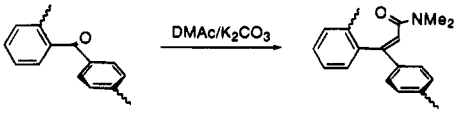


Figure 1. GPC traces of cyclic oligomers: (i) **9c** at different final concentrations; (ii) **28b**; (iii) **28c**, (iv) **28c** obtained using the procedure of Fukuyama; (v) 30b.

the structural rigidity and orthogonal orientating configuration of the spirobiindane group of **7a** which promotes cyclization, and hence led to good yields of the cyclic oligomers.[3b]

Formation of Cyclic Oligomers 10 Utilizing Tetraphenyl-Substituted Monomer 6. We encountered difficulty when trying to prepare cyclic oligomers from the tetraphenyl-substituted monomer **6**. This monomer is not very soluble in polar aprotic solvents at room temperature. Hence the high dilution conditions could not be employed in this case, and the yield of cyclic oligomer was comparatively low. The crude product was further purified by Soxhlet extraction with ethyl acetate to obtain low molecular weight cyclic oligomers.

Solvent Effect and Aldol Condensation Side Reaction. We found that use of *N,N*-dimethylacetamide (DMAc), *N*-methyl-2-pyrrolidinone (NMP), and dimethyl sulfoxide (DMSO) in the preparation of cyclic oligomers from nonphenylated monomer **4** failed to give a clean reaction. DMF was demonstrated to be the best solvent for formation of cyclic oligomers. We suspect that undesirable side reactions may have occurred between these solvents and the reactants or the oligomers formed. Based on matrix-assisted laser desorption ionization time-of-flight mass spectrometry (MALDI-TOF-MS)[11] using $AgCF_3CO_2$ as cationization agent and ^1H NMR analysis, we found that when DMAc was used as solvent an aldol condensation reaction took place between the acidic α-methyl group of DMAc and the carbonyl groups of monomer **4** and the oligomers formed (eq 2). We suspect that similar side reactions may also occur with NMP or DMSO. Since DMF does not have any acidic methyl group, the aldol condensation side reaction was avoided.



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The MALDI-TOF-MS spectrum of the materials obtained from monomer **4** and bisphenol **7c** using the cyclization procedure with DMAc as solvent is shown in Figure 2i. Instead of giving the desired mass/charge (*m/e*) signals for cyclic oligomers, it gave signals at 1265, 1845, 2425, 3004, 3583, and 4163 Da, indicating the presence of oligomers which are aldol condensation adducts **11** between oligomers and DMAc.

Examination of the ^1H NMR spectrum of the same materials revealed two pieces of important information indicating the presence of the condensation products **11** described above. The first one is the signals at 6.3 ppm,

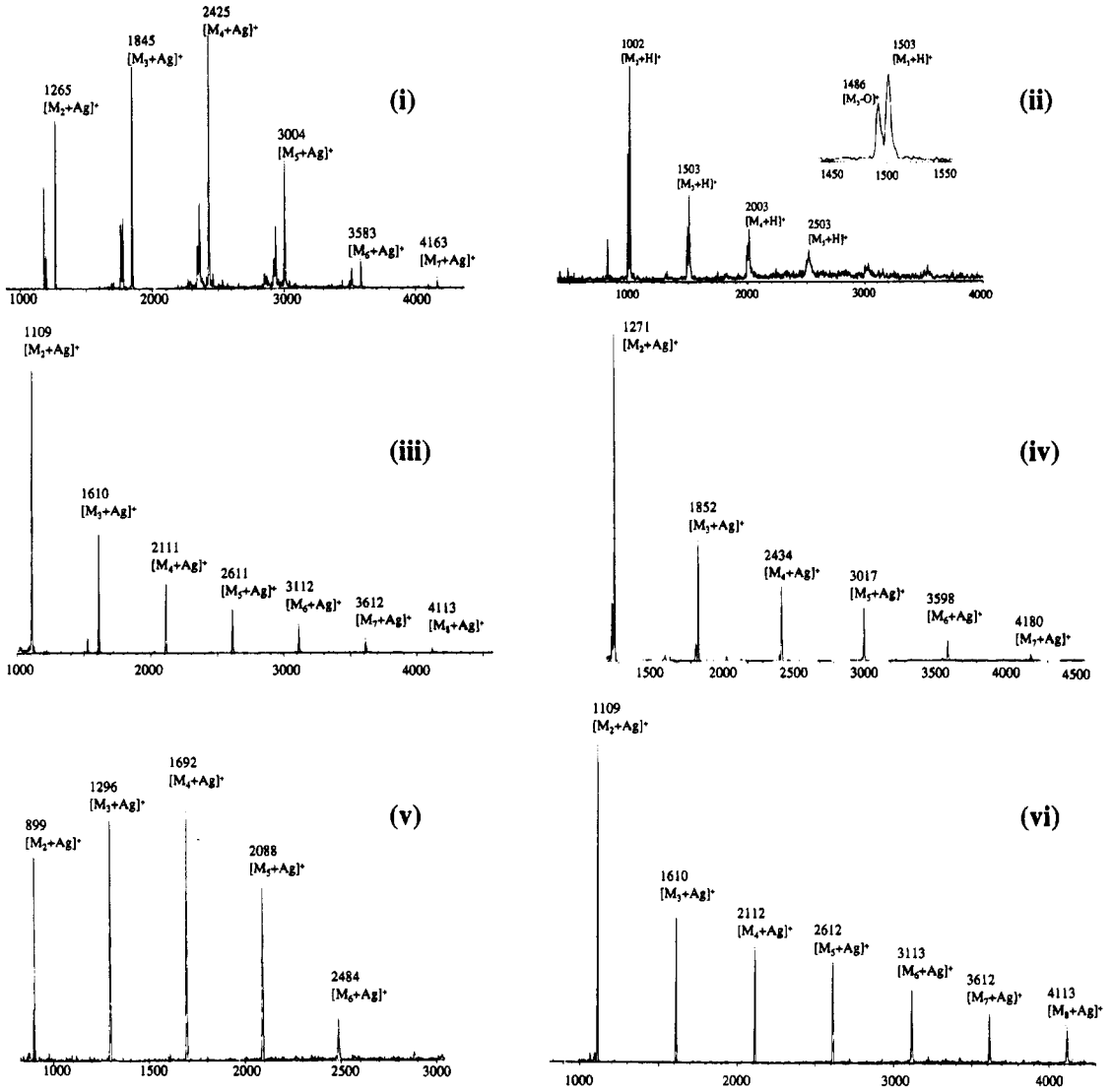
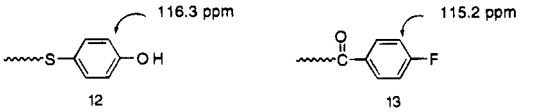


Figure 2. MALDI-TOF-MS spectra of (i) the materials obtained from monomer **4** and bisphenol **7c** when DMAc was used as solvent, (ii) cyclic oligomer **8b** using gentisic acid as matrix, (iii) **8b** using dithranol as matrix and $AgCF_3CO_2$ as cationization agent, (iv) cyclic isoquinoline **24c**, (v) cyclic oligomer **28b**, (vi) cyclic oligomer **30b**.

which correspond to the olefinic proton (H_a) of the aldol adduct **11**. The second one is signals in the region of 2.5−3 ppm coresponding to the *N*-methyl proton of the aldol adducts **11**. The integration is also consistent with one ketone group of the 1,2-dibenzoylbenzene moiety being condensed with DMAc per repeating unit.

In our procedure, the reactants were influxed slowly into the reaction vessel containing solvent and base; therefore, this inevitably created a situation in which the oligomers formed were in contact with excess base, hence resulting in the formation of the Aldol adducts. We found no problems in the preparation of cyclic oligomers from the diphenyl and tetraphenyl monomers **5** and **6** using DMAc as solvent. This may be due to the fact that the extra phenyl substituents create a steric barrier and make the ketone group less accessible.

Cyclic Nature of the Oligomers. The low concentration of end groups detected and the low molecular weight of the materials formed supported the formation of cyclic oligomers. Direct evidence of their cyclic nature was obtained from the mass spectra of the materials prepared. For example, the GPC trace of the cyclic oligomer **8b** shows that it is a low molecular weight material with number-average molecular weight M_n ~1500. This implies an average degree of polymerization (DP) ~ 3. However, examination of the ^{13}C NMR spectrum (Figure 3) shows that no obvious signals from the possible fluoro and phenolic end groups **12** and **13** are detected. Aromatic carbons ortho to the hydroxy and fluoro groups would give very characteristic upfield signals in the region of 116 and 115 ppm, respectively.[12] The use of more sensitive nuclei such as ^{19}F make it possible to detect the presence of end group **13**, which gives rise to signals in the region of −103 to −107 ppm. Fluorobenzene was used as internal standard, and the concentration of the end groups **13** was determined to be one in every 300 structural repeating units in the case of **8b**.



With the advance of soft ionization techniques, especially matrix-assisted laser desorption ionization (MALDI), the accessible mass range of mass spectrometry has been extended considerably. The use of MS as a rapid

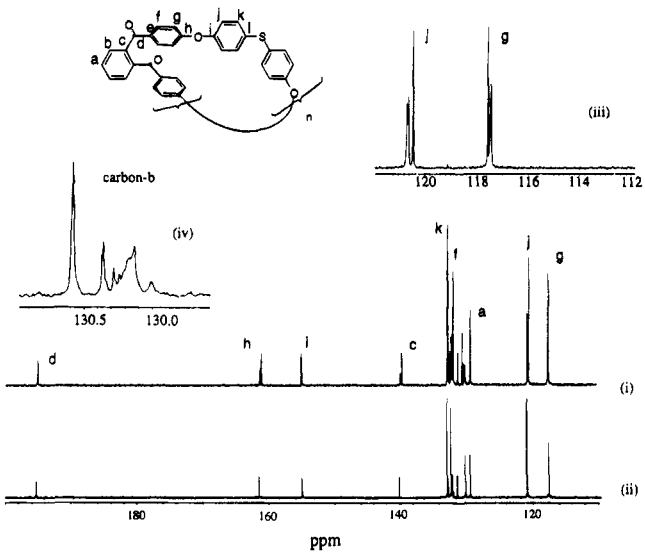


Figure 3. (i) ^{13}C NMR (125 MHz, $CDCl_3$) of cyclic oligomer **8b**, (ii) ^{13}C NMR of corresponding linear polymer of **8b**, and (iii) and (iv) expansions of ^{13}C NMR of cyclic oligomer **8b**.

Table 2. MALDI-TOF-MS Data of Cyclic Oligomer 8b Using Dithranol as Matrix and $AgCF_3CO_2$ as Cationization Agent

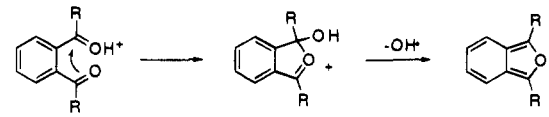
signal (*m/e*)	rel intensity (%)	assignment[a]	calcd *m/e*	deviation (Da)[b]
1109	100	$M_2 + Ag$	1109	0
1610	37	$M_3 + Ag$	1610	0
2111	19	$M_4 + Ag$	2110	+1
2611	11	$M_5 + Ag$	2611	0
3112	7	$M_6 + Ag$	3111	+1
3612	3	$M_7 + Ag$	3612	0
4113	0.5	$M_8 + Ag$	4112	+1

[a] M_x represents the molecular ion with x repeating units; the average molecular weight calculated for repeating unit $C_{32}H_{20}O_4S$ = 500.6. [b] Deviation = (experimental value) − (calculated value).

and accurate method for the detection and identification of complex polymeric mixtures would be of great interest to polymer chemists. Information such as absolute molecular weight distribution, sequence of the repeating units, polymer impurities, and structural information can be obtained.[11]

In MALDI, the samples to be analyzed are mixed uniformly with a substance called a matrix. In an environment where excess matrix is present, the minute sample crystals are surrounded by the matrix crystals (or in an amorphous state). The matrix, which has resonance absorption at the laser wavelength, absorbs the laser energy and causes rapid heating of the matrix for the sample to be vaporized. Reports of the use of this technique for the analysis of polyacrylamide,[13] poly(hydroxyalkanoate)s,[14] polystyrene, and poly(ethylene glycol)s[11] have appeared recently. We found that MALDI-TOF-MS is a simple and rapid method for the detection and identification of oligomeric aryl ethers.

The MALDI-TOF-MS spectrum of **8b**, using 2,5-dihydroxybenzoic acid (gentisic acid) as the matrix material, gives the correct molecular ion peaks for the desired cyclic oligomers, up to pentamer (n = 5), with reasonable signal to noise ratio (Figure 2ii). The expanded scale of the MS spectrum of **8b** shows two signals for each oligomer. For example, signals for the cyclic trimer are located at 1486 and 1503 Da. The signal at 1503 Da corresponds to the protonated molecular ion $[M + H]^+$ peak, and the signal at 1486 Da is due to loss of oxygen through intramolecular cyclization of trimer of **8b** to form isobenzofuran (eq 3). The loss of an oxygen is observed in all other samples containing the 1,2-dibenzoylbenzene moiety. This kind of fragmentation was observed not only in the MALDI method but also in fast atom bombardment (FAB) ionization. We have also observed signals for the potassium adduct $[M_X + K]^+$ and sodium adduct $[M_X + Na]^+$ together with $[M_X + H]^+$ ion signals in the MALDI-TOF mass spectra of other oligomers.



(3)

More recently, we found that using 1,8,9-anthracenetriol (dithranol) as matrix and $AgCF_3CO_2$ as cationization agent gives MS spectra with better signal to noise ratio. For example, the MALDI-TOF-MS spectrum of cyclic oligomer **8b** using these two reagents gives the correct molecular ion signals for the desired oligomers and silver adduct $[M_X + Ag]^+$, up to octamer (n = 8), with excellent signal to noise ratio (Figure 2iii and Table 2). The fragmentation process as shown in eq 3 is also suppressed to give a very simple spectrum.

Composition of the Cyclic Oligomers. Analyses based on GPC and HPLC indicate that the cyclization reaction generates a mixture of oligomeric cyclic (aryl ether ketone)s. The range of oligomerization is principally from degree of polymerization of 2 up to 10. A typical mixture contains 38 wt % cyclic dimer, 16 wt % trimer, 10 wt % tetramer, 7 wt % pentamer, 4 wt % hexamer, and 25 wt % higher homologues. On the other hand, oligomer **8a** contains 37 wt % of cyclic monomer (n = 1). As we have mentioned earlier, the special "bent" configuration of SBI not only facilitates cyclization but also favors the formation of cyclic monomer in high yield as indicated by GPC and MS results. The formation of cyclic monomer was not observed when other bisphenols were used.

Reverse phase HPLC with the appropriate choice of stationary phase, solvents combination, and gradient program is found to be a very useful method to achieve a better separation of the individual oligomers of a cyclic mixture.[15] It gives more precise information on the composition of the cyclic oligomers compared to the use of GPC. In the case of GPC, in order to resolve the individual oligomers in the mixture, three 500 Å columns in series have to be used.[16]

In the HPLC analyses, a combination of a thermodynamically good solvent (THF) and a thermodynamically poor solvent (water) was used. The gradient program was started with a combination of two solvents (60% THF, 40% water) and the volume fraction of THF gradually increased to 85%, and this results in a good separation of the oligomers. We found that oligomers with molecular weight up to 5000 can be separated (Figure 4).

^{13}C NMR of the materials also provides information on the composition of materials. It was found that in the series of cyclic oligomers **8**, carbons on the diketone moiety are sensitive to the size of the oligomers. For example, using carbon b of cyclic oligomer **8b**, one can differentiate signals from dimer up to pentamer (Figure 3iv).

According to the theory of macrocyclization of condensation polymers developed by Jacobson and Stockmayer (JS theory),[17] the distribution of cyclic species

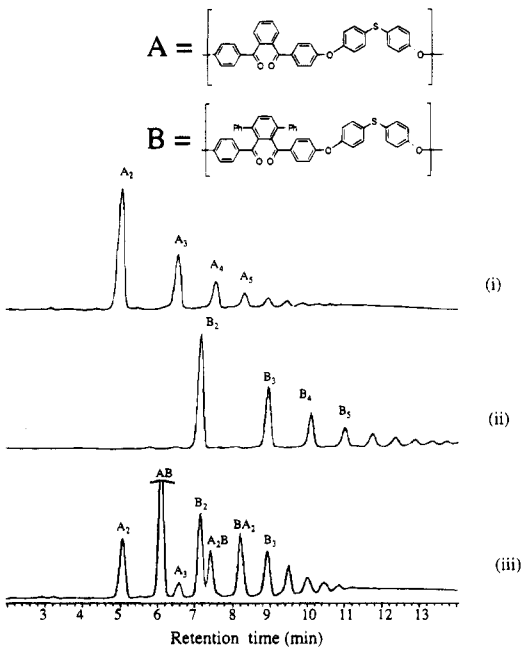


Figure 4. HPLC traces of cyclic oligomers (i) **8b**, (ii) **9b**, and (iii) random cocyclic **14**. A_xB_y indicates a cyclic $(x + y)$-mer component with x repeating units of A and y repeating units of B.

obeys the following equation, which assumes that the distribution of the polymer end-to-end distances in a randomly coiled polymer is given by a Gaussian function.

$$C_n = Bn^{-\gamma}x^n$$

C_n is the concentration of cyclic oligomer with degree of polymerization of n, x is the fraction of reacted end groups of the chains and B is a constant depending on the chemical nature of the molecule and the solvent. For a very high extent of reaction in a system, x will approach unity. Therefore a plot of $\ln(C_n)$ vs $\ln(n)$ will result in a straight line with a slope of $-\gamma$, where $\gamma = 2.5$ according to JS theory prediction.

Based on the weight percent of the oligomers obtained by HPLC analyses, we calculated the C_n for each degree of polymerization (Table 3). We found that good linear plots were obtained for the oligomers. Some examples of the results are shown in Figure 5i. The γ values for our system are higher than 2.5. This indicates that the yields of cyclic oligomers apparently decrease upon increasing molecular weight more rapidly than predicted by JS theory. We believe that the high value of γ compared to that predicted by Jacobson and Stockmayer may be due to the fact that an influxion method, instead of a batchwise procedure, was used for the preparation of the cyclic oligomers. Hence the creation of the pseudo-high dilution condition may favor the formation of smaller ring size cyclic oligomers as a result of dilution beyond a critical concentration as suggested by JS theory. An experiment was carried out to prepare cyclic oligomer **9b** by a batch process for an extended period (18 h) so that ring–chain equilibrium was allowed to build up, in order to satisfy the conditions in the JS theory (Table 3). In this case we obtain a value $\gamma = 2.4$, which is in good agreement with the JS theory within experimental error (Figure 5ii).

Thermoanalyses of Cyclic (Ether Ketone) Oligomers. The glass transition temperature (T_g) and melt temperature (T_m) of the cyclic oligomers were determined by differential scanning calorimetry (DSC) at a heating rate of 20 °C/min (Table 1). It was found that most of the cyclic oligomers are crystalline. Usually, for the first scan, a heat of crystallization was observed, followed by the melting endotherm. For example, a DSC trace of cyclic oligomer **8c** is shown in Figure 6. It was found that the T_gs of the cyclic oligomers are in general 10–20 °C lower than those of the corresponding linear high molecular weight polymers. It is known that the corresponding linear high molecular weight polymers are amorphous.[1] The detection of T_m in most of the cyclic oligomers may be attributed to the fact that a high weight percentage of cyclic dimers is present in the oligomeric mixture, and these dimers crystallize readily.

It was found that the diphenyl-substituted cyclic oligomers **9** have very high T_ms. For instance, **9c** has a T_m above 450 °C and this cyclic oligomer is relatively insoluble in chloroform. However, replacement of the

Table 3. Weight Percent (W_n) and Concentration (C_n) of Cyclic Oligomers

	8b (influxion method)[a]		**8c** (influxion method)[a]	
n	W_n (%)	C_n (mM)	W_n (%)	C_n (mM)
2	47.5	9.5	47.7	9.5
3	21.2	2.8	20.8	2.8
4	10.4	1.0	10.7	1.1
5	5.5	0.4	5.9	0.5
6	3.4	0.2	4.1	0.3
γ	3.4		3.3	
	9b (influxion method)[a]		**9b** (batch method)[b]	
n	W_n (%)	C_n (mM)	W_n (%)	C_n (mM)
2	38.7	7.7	26.2	5.2
3	21.8	2.9	13.6	1.8
4	12.1	1.2	9.5	1.0
5	6.8	0.5	7.2	0.6
6	5.1	0.3	5.2	0.4
γ	2.9		2.4	

[a] The experimental conditions for the influxion method are the same as those of the general synthesis of the cyclic oligomers in the Experimental Section. [b] The same conditions as the influxion method, except all the reactants were added to the reaction vessel at the beginning of the reaction, and it was allowed to reflux for 18 h to reach ring–chain equilibrium.

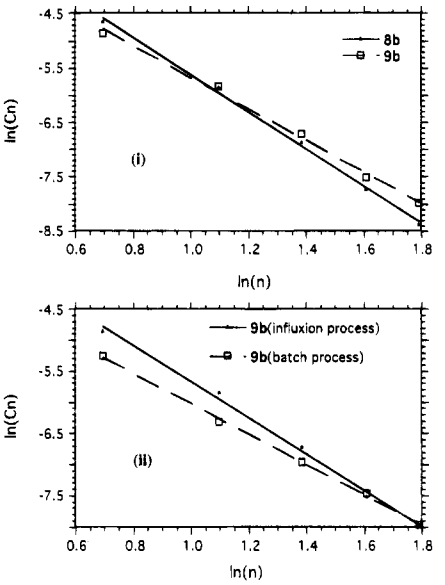


Figure 5. Plot of $\ln(C_n)$ against $\ln(n)$ of (i) cyclic oligomers **8b** and **9b** obtained by influxion method and (ii) cyclic oligomer **9b** obtained by an influxion method and a batch method.

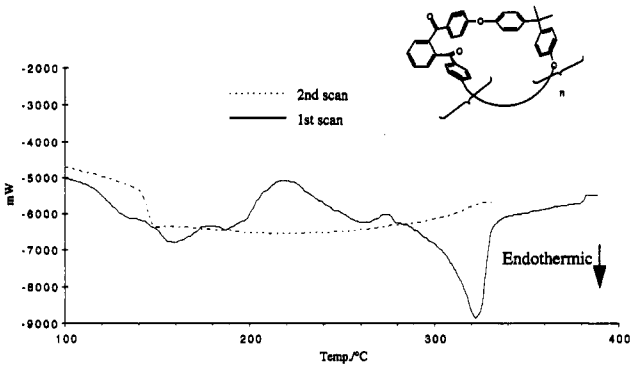
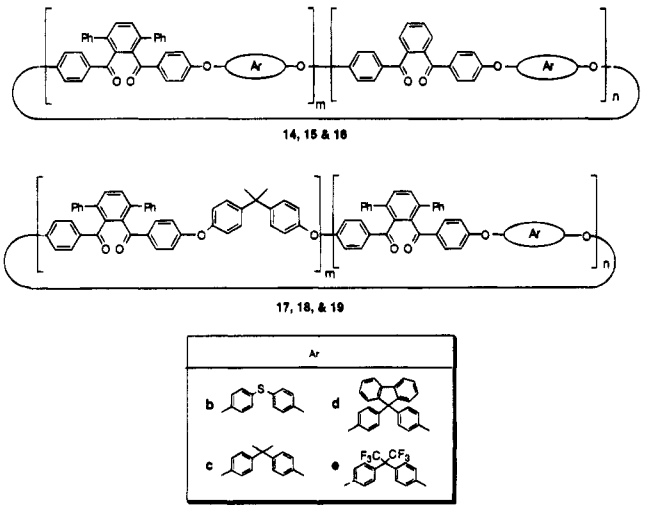


Figure 6. DSC traces of cyclic oligomer **8c**.

BPA moiety with the BPP moiety, which has a flexible diethyl group, results in cyclic oligomers **9f**, in which T_m is lowered to 412 °C, and it is readily soluble in chloroform. Replacing the BPA moiety in **9c** with the hexafluoro-BPA moiety results in cyclic oligomer **9e**. It has a T_g comparable to that of **9c** but the T_m is dramatically reduced to 363 °C, and it is readily soluble in chloroform.

Synthesis of Random Cocyclic Oligomers. We found that some of these cyclic materials are highly crystalline and have high T_ms. The high melting temperature of these cyclic oligomers would be a handicap from a processing point of view. One possible way to reduce the crystallinity and reduce the T_m of the cyclic materials is to prepare random cocyclic oligomers. For example, we applied the same synthetic conditions as in the preparation of the homocyclic oligomers and prepared random cocyclic oligomers **14**, **15**, and **16** by condensing bisphenols with a mixture of difluoro monomers **4** and **5** in various proportions (Table 1). Random cocyclic oligomers **17**, **18**, and **19** were also prepared from difluoro monomer **5** with a mixture of two bisphenols (Table 1). All random cocyclic materials, except **19**, were found to be amorphous. In the case of **19**, crystallinity was found, but the T_m was lower than the T_ms of the homocyclic oligomers **9c** and **9e**.



A HPLC of random cocyclic oligomers **14** is shown in Figure 4iii. Early members of the cyclic mixture can be identified by comparing with HPLC traces of cyclic oligomers **8b** and **9b**. The MALDI-TOF-MS of **14** is shown in Figure 7. The upper detection limit is low compared to that for the homocyclic materials. Only signals up to trimer have reasonable signal to noise ratio. This is attributed to the fact that the cocyclic

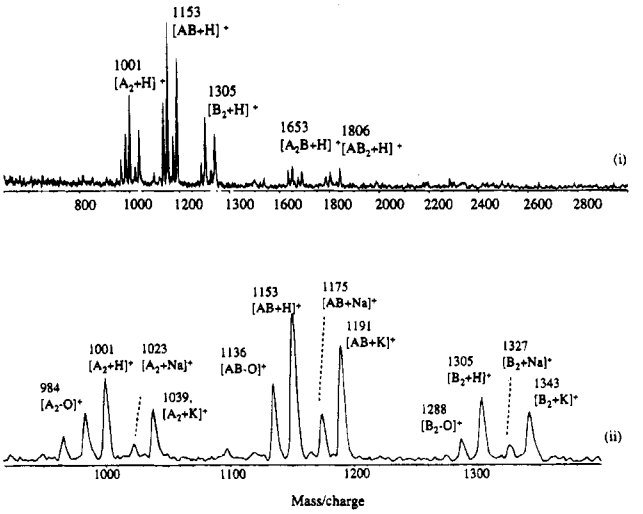
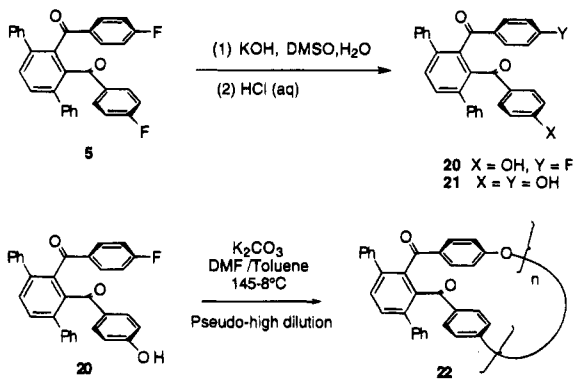


Figure 7. MALDI-TOF-MS spectrum of random cocyclic **14**.

Scheme 2



mixture contains more oligomeric components than the homocyclic mixture. For example, in the case of **14**, the number of possible combinations of cyclic oligomeric components with n repeating units is equal to $n + 1$. Hence, there will be three molecular ion signals for the dimer, four for the tetramer, and so on. The total available charge produced during MALDI will be distributed over a very large number of different ions and hence lead to the low upper detection limit for cocyclic materials. The formation of both potassium and sodium adducts complicates the situation even more.

Synthesis of Cyclic (Aryl Ether Ketone) Using an Unsymmetrical AB-Type Monomer. Cyclic oligomers **8**, **9**, and **10** were obtained by an AA + BB approach where two symmetrical monomers, difluoro monomers **4**, **5**, and **6** and bisphenols **7**, were condensed together to form the desired oligomers (Scheme 1). We have also studied the synthesis of cyclic (aryl ether ketone) by a different synthetic approach in which an unsymmetrical AB-type fluoro–hydroxy monomer **20** was used to prepared cyclic oligomer **22** (Scheme 2).

The fluoro–hydroxy monomer **20** was conveniently prepared by partial hydrolysis of the difluoro monomer **5** with KOH in DMSO and water solution (Scheme 2). In the hydrolysis reaction 1.5 equiv of KOH was used; therefore the reaction only consumed 50% of the starting materials, as indicated by HPLC. The reason for using less than the stoichiometric amount of KOH is to suppress the formation of dihydroxy compound **21**, which is quite difficult to separate from the desired product **20**. We found that the use of 1.5 equiv of KOH gives a good conversion (~50% conversion) of difluoro compound **5** to fluoro–hydroxy compound **20** while

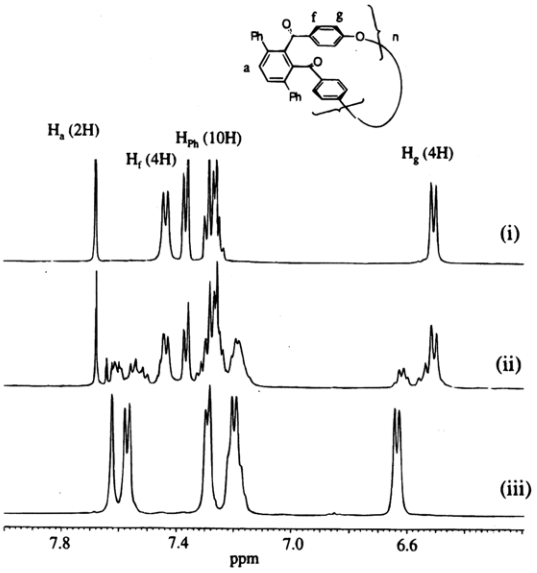


Figure 8. ^{1}H NMR (500 MHz, $CDCl_3$) of (i) cyclic dimer **22** (n = 2), (ii) cyclic oligomer **22**, and (iii) the corresponding high molecular weight linear polymer of **22**.

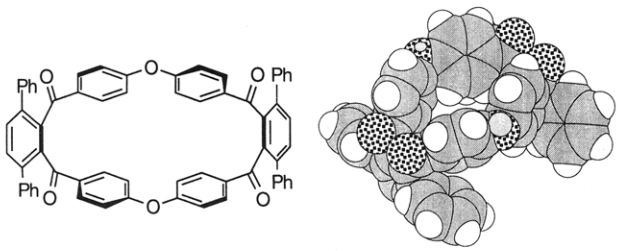


Figure 9. 3D model of dimer **22** (n = 2).

keeping the yield of dihydroxy compound **21** less than 1%. Fluoro–hydroxy monomer **20** can then be easily separated from the starting material **5** by extracting the crude product with aqueous KOH solution.

With the appropriate monomer at hand, we applied similar cyclization conditions. Cyclic oligomer **22** was obtained in 80% isolated yield. It was interesting to find that 55 wt % of the material obained is a 26-member cyclic dimer **22** (n = 2), based on MS, GPC, and ^{1}H NMR (Figure 8) results. This procedure turned out to be an efficient synthesis of macrocycle **22** (n = 2), which may have potentially interesting molecular recognition and catalysis properties for high temperature and hostile environments. The dimer **22** (n = 2) is less soluble in chloroform, while the rest of the cyclic oligomers are readily soluble. Therefore it can be separated easily from the rest of the oligomers and was characterized by spectroscopic methods.

Examination of the molecular model of the dimer **22** (n = 2) indicated that it is free of ring strain and has a very close distance between the ether oxygen atoms, 7.4 Å (Figure 9).[18] The high yield of dimer may be due to the fact that the 1,2-dibenzoylbenzene group can adopt a conformation in which the ends of the benzoyl arms can be brought very close together.

2.2. Synthesis of Cyclic Phthalazine and Isoquinoline Oligomers. Cyclic Phthalazine. Cyclic diketones **8b** and **8c** can be converted to the corresponding phthalazine using hydrazine hydrate and hydrochloric acid with dioxane as solvent.[6] Cyclic oligomers **8b** and **8c** are soluble in refluxing dioxane, the resulting products precipitate out of the reaction mixture, and this facilitates the isolation of the phthalazine cyclic oligomer (Scheme 3 and Table 1).

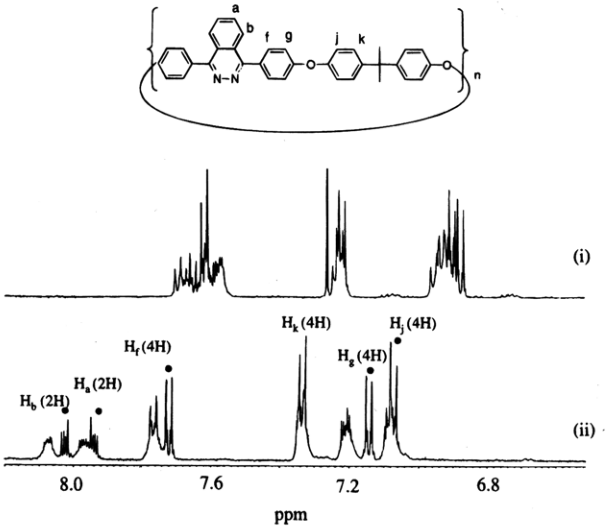
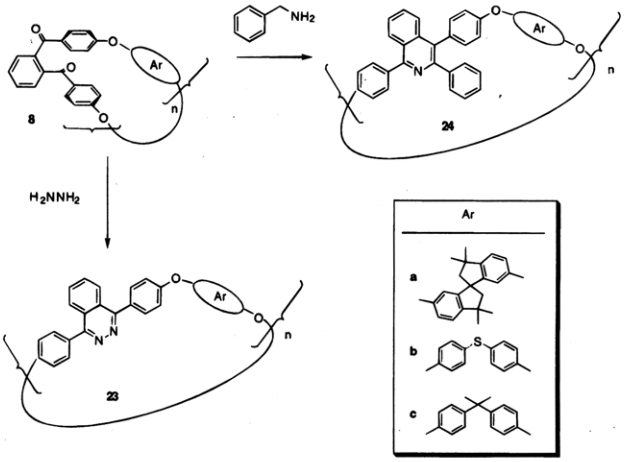


Figure 10. ^{1}H NMR (500 MHz) of (i) cyclic ketone oligomer **8c** in $CDCl_3$ and (ii) cyclic phthalazine oligomer **23c** in DMSO-d_6; the solid circles indicate the signals from the cyclic dimer (n = 2) of **23c**.

Scheme 3



^{1}H NMR spectra of cyclic phthalazine oligomer **23c** and cyclic ketone oligomer **8c** are shown in Figure 10. After transformation, proton signals of the dimer become well separated from the rest of the oligomers as indicated in Figure 10.

In the case of the preparation of cyclic phthalazine **23a** from **8a**, the cyclic monomer of **8a** has to be removed first. The condensation of hydrazine with the cyclic monomer of **8a** did not result in the desired cyclic phthalazine cyclic monomer of **23a** (n = 1); instead undesirable hydrazides **25** and **26** were obtained as shown in Scheme 4 according to FAB-MS analysis. Examination of a molecular model of the cyclic monomer of **23a** (n = 1) (Figure 11) reveals that it is a highly strained macrocycle. The two phenyl arms on the phthalazine moiety are forced to be bent inward. This may explain why the cyclic monomer of **23a** (n = 1) was not obtained.

Removal of the cyclic monomer of **8a** (n = 1) from the rest of the oligomers **8a** can be achieved by selective precipitation, since **8a** (n = 1) has a lower solubility in chloroform. ^{1}H NMR clearly indicated that the cyclic monomer can be reduced down to ~3 wt %, as the proton signals of **8a** (n = 1) are well separated from the other signals (Figure 12). The resulting cyclic phthalazine oligomers **23a** obtained were treated with acetic acid and sodium nitrite to convert the small amount of

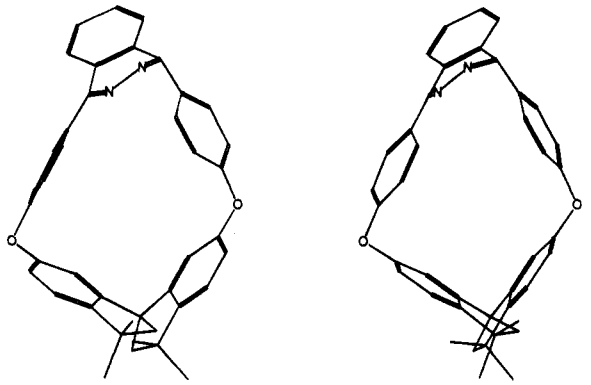


Figure 11. 3D models of cyclic monomer of **23a** (n = 1).

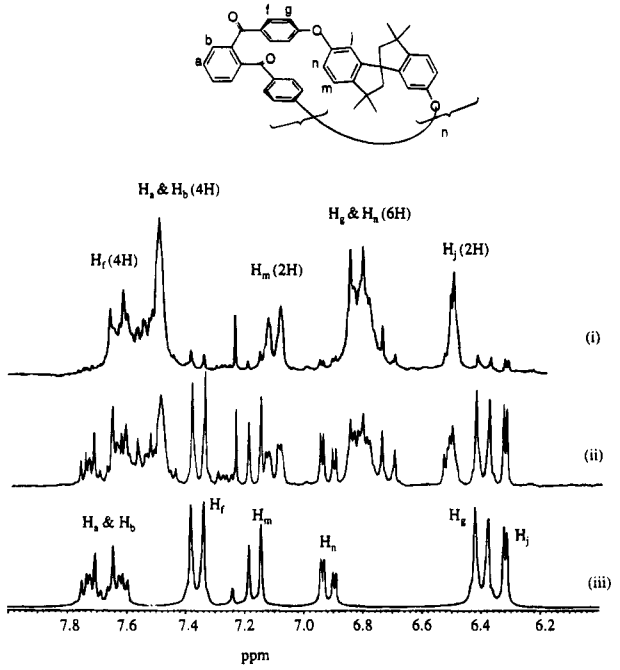
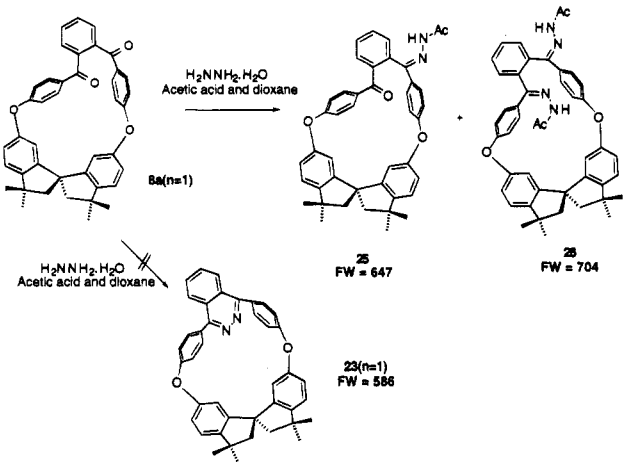


Figure 12. ^{1}H NMR (200 MHz, $CDCl_3$) of (i) cyclic oligomer **8a** with **8a** (n = 1) depleted, (ii) cyclic oligomer **8a** as prepared, and (iii) cyclic monomer **8a** (n = 1).

Scheme 4



undesirable hydrazides **25** and **26** back to cyclic monomer **8a** (n = 1).[19]

Cyclic Isoquinolines. Treating the oligomer **8c** with benzylamine in the presence of the strong base 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) under reflux conditions in chlorobenzene resulted in the cyclic isoquinoline oligomer **24c** in 30 h (Scheme 3 and Table 1).[7] A

Scheme 5

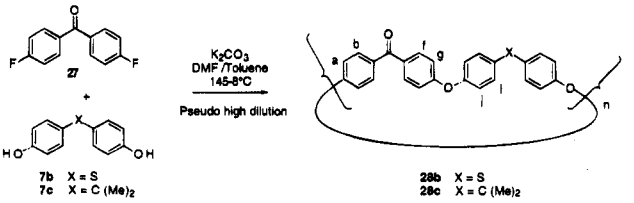


Table 4. Cyclic Oligomer Distribution (wt %)

n	28b	28c	30b
2	56	39	17
3	23	15	10
4	12	8	7
5	6	5	6
>5	1	33	60

Table 5. Comparison of Cyclization Conditions for Cyclic Oligomer

	cyclic oligomer **28c**		cyclic oligomer **30**	
	Fukuyama	present work	Mullins	present work
addition time (h)	3	8	6	0
total reaction time (h)	8	16	24	16
final reactant concn (mM)	80	40	10	40
M_n (kg/mol)	2.5	1.3		
M_w (kg/mol)	32	6		

MALDI-TOF-MS spectrum of **24c** is shown in Figure 2iv. Signals up to n = 7 were detected. Both phthalazine and isoquinoline oligomers are very insoluble in chloroform and DMSO. The T_gs are not apparent in the DSC trace, and we believe that the materials are highly crystalline and have T_ms beyond the decomposition temperatures.

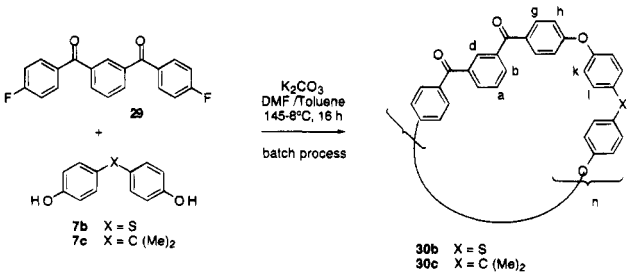
2.3. Cyclic (Aryl Ether Ketone)s from Aromatic Difluorides with Different Geometrical Constraints. Cyclic (Aryl Ether Ketone)s from Difluorobenzophenone 27. In order to further explore the synthetic utility of our cyclization procedure, we employed difluorobenzophenone **27** for the preparation of cyclic (aryl ether ketone). It was found that difluorobenzophenone **27** condensed readily with bisphenols to give high yields of cyclic oligomers **28b** and **28c** with our cyclization conditions (Scheme 5 and Table 1). The GPC of oligomer **28c** has a typical distribution similar to that of the 1,2-dibenzoylbenzene-containing cyclic oligomer **8** (Table 4 and Figure 1iii). On the other hand, the GPC of cyclic oligomer **28b** indicted that only very low molecular weight oligomers were formed; oligomers with DP > 7 were not observed (Table 4 and Figure 1ii).

The cyclic nature of the benzophenone-containing cyclic oligomers **28b** and **28c** were further supported by the MALDI-TOF-MS spectra, which gave the desired signals from dimer to hexamer (Figure 2v).

Fukuyama has reported the synthesis of cyclic oligomer **28c** in his US patent.[20] He employed a similar synthetic method, except that DMSO was used instead of DMF as solvent. He reported a shorter total reaction time and higher final reactants concentration compared to our synthetic conditions (Table 5). We have repeated his experiment and found that the yield of cyclic oligomer **28c** was low compared to our method, in which ~50 wt % of the product consisted of high molecular weight polymer as indicated by GPC analysis (Figure 1iv).

Cyclic (Aryl Ether Ketone) from 1,3-Bis(4-fluorobenzoyl)benzene (29). We have attempted to pre-

Scheme 6



pare cyclic (aryl ether ketone) **30b** from 1,3-bis(4-fluorobenzoyl)benzene (**29**) (an isomeric analogue of difluoro monomer **4**) and bisphenol **7b** (Scheme 6). However, 1,3-bis(4-fluorobenzoyl)benzene (**29**) is not readily soluble in DMAc or DMF; therefore, a batch process instead of pseudo-high dilution conditions was employed. MALDI-TOF-MS (Figure 2vi) analysis indicated that this procedure yields cyclic oligomers; however, the yield is low as indicated by the GPC, where a considerable amount of high molecular weight material is also obtained (Figure 1v and Table 4).

Mullins et al. have reported the preparation of cyclic oligomer **30c** from difluoro monomer **29** with BPA **7c** in their US patent.[21] In their procedure, they condensed difluoro monomer **29** with BPA **7c** to give cyclic oligomer **30c** in 60% yield. They employed NaOH as base and DMSO as solvent. They employed the pseudo-high dilution method by preparing a dilute solution of **29** (125 mM). The reactants were delivered into the reaction vessel over a period of 6 h, and the reaction mixture was refluxed for another 18 h. The final concentration of reactants was 10 mM when the addition was completed (Table 5). It is obvious that the monomer **29** is not readily soluble in DMSO; therefore they had to prepare a dilute (125 mM) solution of **29** in order to employ the pseudo-high dilution conditions. Furthermore, their final reactant concentration was 4 times lower than that of our reported method. Hence they were able to isolate the monocyclic (DP = 1) from the reaction mixture; however, they did not specify the yield of the monocyclic materials.

3. Conclusions

A synthesis of cyclic (aryl ether ketone) oligomers containing a 1,2-dibenzoylbenzene moiety via the nucleophilic aromatic substitution route has been developed. Chemical transformation of the 1,2-dibenzoylbenzene moiety of these cyclic (aryl ether ketone)s led to the preparation of novel cyclic (aryl ether phthalazine)s and cyclic (aryl ether isoquinoline)s. Cyclic (aryl ether ketone)s derived from 4,4′-difluorobenzophenone can be obtained in high yield with our cyclization procedure. Detailed structural characterization of these novel oligomers by MALDI-TOF-MS, ^{13}C and ^{1}H NMR, GPC, and HPLC confirmed the cyclic nature and revealed the composition of the oligomeric mixtures prepared. MALDI-TOF-MS, which enables the detection of oligomers with mass up to 5000 Da, was shown to be a very powerful tool for the analysis and proof of the cyclic nature of the oligomers. Thermoanalyses show that most of these oligomers exhibit a high degree of crystallinity while their corresponding polymers are amorphous.

4. Experimental Section

Instrumentation. ^{1}H, ^{13}C, and ^{19}F NMR experiments were performed at room temperature on Varian XL-200, Varian XL-300, and Unity 500 NMR spectrometers. Assignment of carbon and proton signals of the cyclic oligomers is according to the labeling scheme shown in Figure 13. $^{1}H-^{1}H$ correlation experiments and $^{1}H-^{13}C$ correlation experiments were performed to make the proton and carbon chemical shift assignments. EI mass spectra were recorded on a DuPont 21-492B spectrometer. Positive ion fast atom bombardment (FAB) mass spectra were recorded on a ZAB 2F HS spectrometer using 3-nitrobenzyl alcohol as a matrix. MALDI spectra were recorded on a Kratos Kompact MALDI-III TOF instrument with a maximum laser output of 6 mV at a wavelength of 337 nm. The ions produced from each laser shot were accelerated to 20 keV into a 1 m drift region. The MALDI spectra were recorded at positive linear or reflection mode. Sample concentrations were approximately 10–50 nmol/μL, and 2,5-dihydroxybenzoic acid or dithranol was used as a matrix and $AgCF_3CO_2$ as a cationization agent. Equal volumes were mixed, and 0.6 μL was placed on the target slide and air-dried.

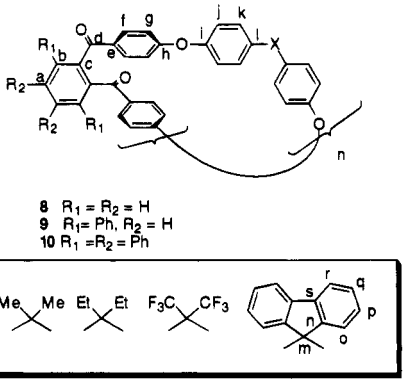


Figure 13. Labeling for ^{1}H and ^{13}C assignment of cyclic oligomers.

HPLC analyses were performed on a DuPont Model 410 pump, ISS-100 autoinjector, and LC-235 diode array detector. A THF/water gradient was used for the elution of product on a C-8 reverse phase column (4.6 × 256 mm). The gradient program was as follows: step 1, 60–84% THF over 17 min at exponent −2; step 2, 84–100% THF over 1 min at exponent 1; step 3, 100% THF for 6 min; step 4, 100–60% THF over 2 min (recycle). GPC analyses were performed on a Waters 510 HPLC equipped with Phenogel 5μ columns (7.8 × 300 mm), one linear and three 500 Å arranged in series, with chloroform as eluent and UV detection (254 nm). Thermoanalyses were obtained on Seiko 220 DSC and 220 TGA/DTA instruments.

Starting Materials. Difluoro monomers **4**, **5**, and **6** were prepared according to the published procedure,[5] 4,4′-difluorobenzophenone (**27**) was obtained from Aldrich Chemical Co., and 1,3-bis(4-fluorobenzoyl)benzene (**29**) was prepared according to the published procedure.[22] 2,2′,3,3′-Tetrahydro-3,3,3′,3′-tetramethyl-1,1′-spiro[1*H*-indene]-6,6′-diol (**7a**) and 3,3′-bis(4-hydroxyphenyl)pentane (**7f**) were kindly supplied by the General Electric Co. 4,4′-Thiodiphenol (**7b**) and 2,2-bis(4-hydroxyphenyl)propane (**7c**) were obtained from Aldrich Chemical Co. 9,9-Bis(4-hydroxyphenyl)fluorene (**7d**) and 2,2-bis(4-hydroxyphenyl)hexafluoropropane (**7e**) were obtained from Kennedy & Klim, Inc., NJ. Hydrazine hydrate and DBU were obtained from Aldrich Chemical Co.

Synthesis of *cyclo*-Poly[oxy-6,6′-(3,3,3′,3′-tetramethyl-2,2′,3,3′-tetrahydro-1,1-spirobiindenylene)oxy-1,4-phenylenecarbonyl-1,2-phenylenecarbonyl-1,4-phenylene] (8a). The cyclization reaction was conducted in a 500 mL three-neck round-bottom flask equipped with a nitrogen inlet, thermometer, Dean–Stark trap, and condenser. 1,2-Bis(4-fluorobenzoyl)benzene (**4**) (8.0 g, 25 mmol), SBI (**7a**) (7.67 g, 25 mmol), potassium carbonate (7.52 g, 54.4 mmol), DMAc (240 mL), and toluene (120 mL) were added. The resulting mixture was refluxed for 6 h, keeping the temperature in the range 138–140 °C. The reaction mixture was cooled and filtered to remove the salts. The solution was then poured into methanol (1 L). The desired cyclic oligomer **8a** (80% yield, 12.2 g) precipitated out as a white powder and was collected by suction

filtration. The product was dried in a vacuum oven (120 °C) for 12 h.

Isolation of Cyclic Monomer 8a ($n = 1$). Cyclic monomer of **8a** ($n = 1$) (0.64 g) was separated from a mixture of cyclic oligomer **8a** (3.5 g) by flash column chromatography using a petroleum ether/diethyl ether (1:1) mixed solvent system: mp 352–3 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.39 (s, 12H, Me), 2.16 (d, J = 13 Hz, 2H, CH_2), 2.47 (d, J = 13 Hz, 2H, CH_2), 6.33 (d, J = 2 Hz, 2H, H-j), 6.40 (d, J = 9 Hz, 4H-g), 6.93 (dd, J = 2, 8 Hz, 2H, H-n), 7.18 (d, J = 8 Hz, 2H, H-m), 7.36 (d, J = 9 Hz, 4H, H-f), 7.69 (m, 4H, H-a,b); ^{13}C NMR (67.80 MHz, $CDCl_3$) δ 30.43 (Me), 31.97 (Me), 43.90 (CH_2), 57.93, 58.97, 116.18 (C-g), 118.13 (C-j), 121.82 (C-n), 123.78 (C-m), 130.02 (C-b), 131.33 (C-a), 131.61 (C-f), 132.00 (C-e), 139.36 (C-c), 150.63, 153.30, 154.75, 164.75, 164.40, 195.17 (C=O); MS (FAB) m/e 591 (MH^+). The labeling scheme for the carbon and proton assignments of cyclic monomer **8a** ($n = 1$) can be found in Figure 12.

General Procedure for Synthesis of Cyclic Oligomers. The synthesis of cyclic oligomer **8b** is used as an example. The cyclization reaction was conducted in a 3 L three-neck round-bottom flask equipped with a nitrogen inlet, thermometer, Dean–Stark trap, and condenser. The flask was charged with 1.5 L of DMF, 150 mL of toluene, and 150 g of potassium carbonate. The solution was mechanically stirred and heated to reflux. The temperature range of the refluxing solution was 145–8 °C. A solution of 4,4′-thiodiphenol (**7b**) (16.26 g, 74 mmol) and 1,2-bis(4-fluorobenzoyl)benzene (**4**) (24 g, 74 mmol) in 120 mL of DMF was added over an 8 h period via a syringe pump. After the addition was completed, the resulting solution was refluxed for another 8 h. The reaction mixture was cooled and filtered to remove all the salt. The solvent was then removed from the filtrate under reduced pressure. The residue was dissolved in 300 mL of hot chloroform and filtered through a layer of Celite. The chloroform solution was concentrated to 100 mL and added to vigorously stirred methanol (300 mL) via a dropping funnel. The desired oligomers precipitated as a pale-green solid in the methanol. The precipitate was filtered and dried in a vacuum oven (120 °C) for 12 h. The yield of **8b** was 34 g (90% yield). A similar procedure was applied for the preparation of cyclic oligomers **8c**, **8d**, **9b**, **9c**, **9d**, **9e**, **9f**, **28b**, and **28c**. Yields of the products are shown in Table 1.

***cyclo*-Poly(oxy-1,4-phenylenethio-1,4-phenyleneoxy-1,4-phenylenecarbonyl-1,2-phenylenecarbonyl-1,4-phenylene) (8b):** ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.88–7.00 (m, 8H, H-g,j), 7.30–7.38 (m, 4H, H-k), 7.55–7.75 (m, 8H, H-a,b,f); ^{13}C NMR (125 MHz, $CDCl_3$) δ 117.5 (C-g), 120.5 (C-j), 129.3 (C-a), 130.0–130.5 (C-b), 131.2 (C-l), 131.9–132.5 (C-e,f), 132.8 (C-k), 139.8 (C-c), 155.0 (C-i), 161.1 (C-h), 195.2 (C-d).

***cyclo*-Poly(oxy-1,4-phenyleneisopropylidene-1,4-phenyleneoxy-1,4-phenylenecarbonyl-1,2-phenylenecarbonyl-1,4-phenylene) (8c):** ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.70 (s, 6H, Me), 6.85–6.96 (m, 8H, Hg,j), 7.20–7.25 (m, 4H, H-k), 7.55–7.72 (m, 8H, H-a,b,f); ^{13}C NMR (125 MHz, $CDCl_3$) δ 30.9 (Me), 42.3 (CMe_2), 117.0 (C-g), 119.5 (C-j), 128.3 (C-k), 129.3 (C-a), 130.0–130.4 (C-b), 131.6–132.2 (C-e,f), 139.8 (C-c), 146.8 (C-l), 153.2 (C-i), 161.9 (C-h), 195.2 (C-d).

***cyclo*-Poly(oxy-1,4-phenylene-9,9-fluorenylidene-1,4-phenyleneoxy-1,4-phenylenecarbonyl-1,2-phenylenecarbonyl-1,4-phenylene) (8d):** ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.84–6.94 (m, 8H, H-g,j), 7.18–7.25 (m, 4H, H-k), 7.25–7.46 (m, 6H, H-o,p,q), 7.52–7.64 (m, 4H, H-a,b), 7.64–7.72 (m, 4H, H-f), 7.74–7.82 (m, 2H, H-r); ^{13}C NMR (125 MHz, $CDCl_3$) δ 64.4 (C-m), 117.0–117.4 (C-g), 119.6 (C-j), 120.3 (C-r), 126.0 (C-o,p,q), 127.7 (C-o,p,q), 127.9 (C-o,p,q), 129.2 (C-a), 129.6 (C-k), 130.0–130.3 (C-b), 131.7–132.3 (C-e,f), 140.0 (C-c), 142.0 (C-l), 150.8 (C-n,s), 154.2 (C-i), 161.6 (C-h), 195.2 (C-d).

***cyclo*-Poly[oxy-1,4-phenylenethio-1,4-phenyleneoxy-1,4-phenyleneoxy-1,4-phenylenecarbonyl(3,6-diphenyl-1,2-phenylene)carbonyl-1,4-phenylene] (9b):** ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.70–6.76 (m, 4H, H-g), 6.76–6.86 (m, 4H, H-j), 7.12–7.22 (m, 6H, H-Ph), 7.22–7.32 (m, 8H, H-k and H-Ph), 7.50–7.62 (m, 6H, H-a,f); ^{13}C NMR (125 MHz, $CDCl_3$) δ 117.4 (C-g), 120.3 (C-j), 127.6 (C-Ph), 128.2 (C-Ph), 129.1 (C-Ph), 131.0 (C-a), 132.0 (C-f), 132.5 (C-l), 132.7 (C-k), 133.0 (C-e), 139.0 (C-b,c and C-Ph), 139.3 (C-b,c and C-Ph), 139.5 (C-b,c and C-Ph), 155.3 (C-i), 160.7 (C-h), 197.3 (C-d).

***cyclo*-Poly[oxy-1,4-phenyleneisopropylidene-1,4-phenyleneoxy-1,4-phenylenecarbonyl(3,6-diphenyl-1,2-phenylene)carbonyl-1,4-phenylene] (9c):** ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.70 (s, 6H, Me), 6.64–6.75 (m, 4H, H-g), 6.75–6.84 (m, 4H, H-j), 7.12–7.25 (m, 10H, H-k and H-Ph), 7.25–7.35 (m, 4H, H-Ph), 7.50–7.60 (m, 6H, H-a,f); ^{13}C NMR (125 MHz, $CDCl_3$) δ 30.0 (Me), 42.3 (CMe_2), 116.9 (C-g), 119.3 (C-j), 127.5 (C-Ph), 128.2 (C-Ph and C-k), 129.1 (C-Ph), 130.8 (C-a), 131.9 (C-f), 132.5 (C-e), 139.0 (C-b,c and C-Ph), 139.4 (C-b,c and C-Ph), 146.5 (C-l), 153.4 (C-i), 161.5 (C-h), 197.0 (C-d).

***cyclo*-Poly[oxy-1,4-phenylene-9,9-fluorenylidene-1,4-phenyleneoxy-1,4-phenylenecarbonyl(3,6-diphenyl-1,2-phenylene)carbonyl-1,4-phenylene] (9d):** ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.68–6.74 (m, 4H, H-g), 6.74–6.78 (m, 4H, H-j), 7.12–7.42 (m, 20H, ArH), 7.50–7.62 (m, 6H, H-a,f), 7.74–7.82 (m, 2H, H-r); ^{13}C NMR (125 MHz, $CDCl_3$) δ 64.4 (C-m), 117.2 (C-g), 119.4 (C-j), 120.3 (C-r), 126.0 (C-o,p,q), 127.5 (C-o,p,q), 127.7 (C-Ph), 127.8 (C-o,p,q), 128.2 (C-Ph), 129.1 (C-Ph), 129.5 (C-k), 130.9 (C-a), 132.0 (C-f), 132.6 (C-e), 139.0 (C-b,c and C-Ph), 139.3 (C-b,c and C-Ph), 139.5 (C-b,c and C-Ph), 140.0 (C-n,s), 141.7 (C-l), 150.9 (C-n,s), 154.5 (C-i), 161.1 (C-h), 197.1 (C-d).

***cyclo*-Poly[oxy-1,4-phenylene(hexafluoroisopropylidene)-1,4-phenyleneoxy-1,4-phenylenecarbonyl(3,6-diphenyl-1,2-phenylene)carbonyl-1,4-phenylene] (9e):** ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.76–6.82 (m, 4H, H-g), 6.84–6.90 (m, 4H, H-j), 7.12–7.24 (m, 6H, Ph), 7.27–7.38 (m, 8H, H-k and H-Ph), 7.56–7.64 (m, 6H, H-a,f).

***cyclo*-Poly[oxy-1,4-phenylene-3,3-pentanylidene-1,4-phenyleneoxy-1,4-phenylenecarbonyl(3,6-diphenyl-1,2-phenylene)carbonyl-1,4-phenylene] (9f):** ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.62 (m, 6H, CH_3), 2.08 (m, 4H, CH_2), 6.63–6.74 (m, 4H, H-g), 6.74–6.84 (m, 4H, H-j), 7.07–7.32 (m, 14H, H-k and H-Ph), 7.48–7.60 (m, 6H, H-a,f).

***cyclo*-Poly[oxy-1,4-phenylenethio-1,4-phenyleneoxy-1,4-phenylenecarbonyl(3,4,5,6-tetraphenyl-1,2-phenylene)carbonyl-1,4-phenylene] (10b).** The cyclization reaction was conducted in a 100 mL three-neck round-bottom flask equipped with a nitrogen inlet, thermometer, Dean–Stark trap, and condenser. The flask was charged with 80 mL of DMF, 10 mL of toluene, 4,4′-thiodiphenol (**7b**) (0.5 g, 2.29 mmol), difluoro- monomer **6** (1.44 g, 2.29 mmol), and 5 g of potassium carbonate. The solution was magnetically stirred and heated to reflux. The temperature range of the refluxing solution was 145–8 °C. The resulting solution was refluxed for another 16 h. The reaction mixture was filtered while it was still hot to remove the salts. The solvent was then removed from the filtrate under reduced pressure. The residue was extracted with ethyl acetate (50 mL) using a Soxhlet apparatus for 24 h. Evaporation of the ethyl acetate gave the desired oligomer **10b** (700 mg, 36% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.70–7.00 (m, 28H, ArH), 7.22–7.32 (m, 4H, H-k), 7.54–7.64 (m, 4H, H-f).

1-(4-Hydroxybenzoyl)-2-(4-fluorobenzoyl)-3,6-diphenylbenzene (20). 1,2-Bis(4-fluorobenzoyl)-3,6-diphenylbenzene (**5**) (5 g, 10.8 mmol) was dissolved in DMSO (50 mL) followed by the addition of KOH (0.89 g, 15.9 mmol) in water (7.5 mL). The resulting solution was refluxed for 15 min and poured into 1 M HCl (500 mL), giving a precipitate which was filtered. The solid was then dissolved in ether (300 mL) and extracted with 5% KOH solution (2 × 300 mL). The combined KOH layers were acidified with concentrated HCl. The solid precipitate was collected by filtration. Recrystallization of the solid from ethanol gave the desired monomer **20** (2.30 g): mp 251–2 °C; ^{1}H NMR (200 MHz, DMSO-d_6) δ 10.33 (s, 1H), 7.70 (s, 2H), 7.52 (dd, J = 8.6, 5.3 Hz, 2H), 7.37 (d, J = 8.6 Hz, 2H), 7.31–7.17 (m, 10H), 7.05 (dd, J = 8.6 Hz, 2H), 6.59 (d, J = 8.6 Hz, 2H); ^{13}C NMR (67.8 MHz, DMSO-d_6) δ 197.25, 196.52, 167.52, 163.81, 163.09, 140.27, 140.06, 139.93, 139.67, 138.78, 134.94, 134.91, 133.28, 133.12, 133.07, 132.39, 131.94, 129.93, 129.85, 129.78, 129.36, 129.29, 128.76, 128.65, 116.37, 116.05, 115.90; MS (EI) m/e 472 (M^+).

1,2-Bis(4-hydroxybenzoyl)-3,6-diphenylbenzene (21). 1,2-Bis(4-fluorobenzoyl)-3,6-diphenylbenzene (**5**) (5 g, 10.8

mmol) was dissolved in DMSO (50 mL) followed by the addition of KOH (4.8 g, 85.7 mmol) in water (10 mL). The resulting solution was refluxed for 30 min, allowed to cool to room temperature, and neutralized with 1 M hydrochloric acid. The solid precipitate was collected by filtration. Recrystallization of the solid from DMSO gave the desired monomer **21** (4.0 g, 80% yield): mp 370–1 °C; ^{1}H NMR (500 MHz, DMSO-d_6) δ 10.25 (s, 2H), 7.65 (s, 2H), 7.31 (d, J = 8.8 Hz, 4H), 7.17–7.28 (m, 10H), 6.55 (d, J = 7.3 Hz, 4H); ^{13}C NMR (50 MHz, DMSO-d_6) δ 196.95, 163.35, 140.79, 140.06, 139.68, 133.35, 132.13, 130.15, 129.56, 128.86, 116.08; MS (EI) m/e 470.7 (M^+).

***cyclo*-poly[oxy-1,4-phenylenecarbonyl(3,6-diphenyl-1,2-phenylene)carbonyl-1,4-phenylene] (22).** The cyclization reaction was conducted in a 50 mL three-neck round-bottom flask equipped with a nitrogen inlet, thermometer, Dean–Stark trap, and condenser. The flask was charged with 20 mL of DMF, 3 mL of toluene, and 2 g of potassium carbonate. The solution was magnetically stirred and heated to reflux. The temperature range of the refluxing solution was 145–8 °C. A solution of 1-(4-hydroxybenzoyl)-2-(4-fluorobenzoyl)-3,6-diphenylbenzene (**20**) (630 mg, 1.33 mmol) in 5 mL of DMF was added over an 8 h period via a syringe pump. After the addition was completed, the resulting solution was refluxed for another 8 h. The reaction mixture was filtered while hot to remove the salts. The solvent was then reduced to 10 mL under reduced pressure and added into vigorously stirred methanol (30 mL). The desired oligomer **22** precipitated as a white solid in the methanol. The precipitate was filtered and dried in a vacuum oven (120 °C) for 12 h. The yield of **22** was 500 mg (80% yield).

Linear Polymeric Analogue of 22, Poly[oxy-1,4-phenylenecarbonyl(3,6-diphenyl-1,2-phenylene)carbonyl-1,4-phenylene]. The polymerization reaction was conducted in a 50 mL three-neck round-bottom flask equipped with a nitrogen inlet, thermometer, Dean–Stark trap, and condenser. The reaction vessel was charged with difluoro monomer **5** (1.01 g, 2.1 mmol), dihydroxy monomer **21** (1.00 g, 21 mmol), potassium carbonate (0.5 g), DMAc (8 mL), and toluene (4 mL). The resulting mixture was refluxed for 3 h, and the temperature was raised to 165 °C by removing toluene. The reaction mixture was kept at 165 °C for 48 h whereupon the polymer precipitated from the mixture. The reaction mixture was cooled and filtered. The crude product was dissolved in hot NMP (10 mL), filtered, and precipitated into MeOH (50 mL) to yield the desired polymer (1.6 g, 80% yield): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.62 (s, 2H), 7.57 (d, J = 7.5 Hz, 4H), 7.29 (d, J = 7 Hz, 4H), 7.20 (m, 6H), 6.63 (d, J = 7.5 Hz, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 197.40, 159.77, 139.64, 139.30, 139.22, 133.51, 131.86, 131.02, 129.17, 128.23, 127.57, 118.11. M_w = 40 kg/mol; M_n = 16 kg/mol. Inherent viscosity ($CHCl_3$, 25 °C) = 0.33 dL/g.

Isolation of *cyclo*-Bis[oxy-1,4-phenylenecarbonyl(3,6-diphenyl-1,2-phenylene)carbonyl-1,4-phenylene] (22 (n = 2)). The mixture of cyclic oligomer **22** (500 mg) was refluxed with chloroform (5 mL) in a test tube for 2 min, and the hot solution was filtered under suction. The residue was the desired cyclic dimer **22** (n = 2) (200 mg), which was collected and dried in a vacuum oven for 12 h: mp 415 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.68 (s, 2H), 7.44 (d, J = 8.3 Hz, 4H), 7.37 (d, J = 7.8 Hz, 4H), 7.25–7.30 (m, 6H), 6.51 (d, J = 8.3 Hz, 4H); MS(FAB) m/e 905 ($M + H^+$).

***cyclo*-Poly[1,4-phthalazinylene-1,4-phenyleneoxy-6,6′-(3,3,3′,3′-tetramethyl-2,2′,3,3′-tetrahydro-1,1′-spirobiindenylene)oxy-1,4-phenylene] (23a).** Cyclic oligomer **8a** (16 g) was refluxed with 50 mL of chloroform for 30 min. Then the solution was allowed to stand at room temperature for 2 h. At this time the cyclic monomer **8a** (n = 1) was precipitated out and removed by suction filtration. Evaporation of the filtrate gave the desired oligomer mixture (6.5 g) with 3 wt % of cyclic monomer. To a solution of monocyclic depleted cyclic oligomer **8a** (2 g) in dioxane (20 mL) were added hydrazine hydrate (2 mL) and concentrated HCl acid (0.6 mL). The resulting solution was refluxed for 3 h. A green solid precipiated out during the reflux. The solid was filtered and then redissolved in acetic acid (20 mL), followed by the addition of sodium nitrate (3 g). The solution was refluxed for 15 min, coagulated in water (20 mL), and filtered. The residue was redissolved in chloroform and filtered. The chloroform solution was concentrated and then coagulated in methanol (50 mL). The green solid was filtered and dried under vacuum at 120 °C overnight to give the desired product **23a** in 90% yield. M_n = 1.8 kg/mol, M_w = 3.7 kg/mol.

***cyclo*-Poly(1,4-phthalazinylene-1,4-phenyleneoxy-1,4-phenylenethio-1,4-phenyleneoxy-1,4-phenylene) (23b).** To a solution of cyclic oligomer **8b** (2 g) in dioxane (10 mL) were added hydrazine hydrate (0.5 mL) and concentrated HCl acid (0.15 mL). The resulting solution was refluxed for 2 h. A green solid precipitated out during heating. The reaction mixture was diluted with methanol (20 mL), and the green solid was filtered and dried under vacuum for 12 h to give the desired cyclic oligomer **23b** (1.9 g, 95% yield). The same procedure was followed for the synthesis of **23c** from **8c**. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.08 (d, J = 8.3 Hz, 4H, H-j), 7.16 (d, J = 8.3 Hz, H-g of dimer), 7.22 (m, H-g), 7.39 (m, 4H, H-k), 7.76 and 7.80 (d, J = 8.3 Hz, 4H, H-f), 7.83 and 7.87 (m, 2H, H-a), 8.10 and 8.17 (m, 2H, H-b); ^{13}C NMR (125 MHz, $CDCl_3$) δ 118.48 (C-g), 118.80 (C-g), 118.94 (C-g), 119.85 (C-j), 120.05 (C-j), 120.60 (C-j), 125.85 (C-c), 126.49 (C-b), 130.50 (C-e), 131.18 (C-l), 131.34 (C-l), 131.79 (C-f), 131.86 (C-f), 131.98 (C-a), 132.04 (C-a), 132.88 (C-k), 133.06 (C-k), 156.16, 157.96, 158.10, 158.30, 158.54.

***cyclo*-Poly(1,4-phthalazinylene-1,4-phenyleneoxy-1,4-phenyleneisopropylidene-1,4-phenyleneoxy-1,4-phenylene (23c):** ^{1}H NMR (500 MHz, DMSO-d_6) δ 1.68–1.73 (m, 6H, Me), 7.04–7.10 (m, 4H, H-j), 7.14 (d, J = 8.3 Hz, H-g of dimer), 7.20 (m, H-g), 7.30–7.36 (m, 4H, H-k), 7.72 (d, J = 8.3 Hz, H-f of dimer), 7.76 (d, J = 8.3 Hz, H-f), 7.90–8.10 (m, 4H, H-a,b).

***cyclo*-Poly[1,4-(3-phenylisoquinolinylene)-1,4-phenyleneoxy-1,4-phenyleneisopropylidene-1,4-phenyleneoxy-1,4-phenylene] (24c).** To a solution of **8c** (0.5 g) in chlorobenzene (10 mL) were added benzylamine (2 mL) and 1,8-diazabicyclo[5.4.0]undec-7-ene (2 mL). The resulting solution was refluxed for 30 h. The solution was coagulated in methanol (50 mL), filtered, and dried under vacuum for 12 h to give **24c** as a green solid in 80% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.68–1.73 (m, 6H, Me), 6.92–7.00 (m, 2H), 7.00–7.12 (m, 4H), 7.12–7.40 (m, 11H), 7.40–44 (m, 2H), 7.45–7.56 (m, 1H), 7.56–7.65 (m, 1H), 7.70–7.82 (m, 3H), 8.14–8.24 (m, 1H).

***cyclo*-Poly(oxy-1,4-phenylenethio-1,4-phenyleneoxy-1,4-phenylenecarbonyl-1,4-phenylene) (28b).** The cyclization reaction was conducted in a 3 L three-neck round-bottom flask equipped with a nitrogen inlet, thermometer, Dean–Stark trap, and condenser. The flask was charged with 50 mL of DMF, 5 mL of toluene, and 1 g of potassium carbonate. The solution was mechanically stirred and heated to reflux. The temperature range of the refluxing solution was 145–8 °C. A solution of 4,4′-thiodiphenol (**7b**) (0.5 g, 2.29 mmol) and difluorobenzophenone (**27**) (0.5 g, 2.29 mmol) in 5 mL of DMF was added over an 8 h period via a syringe pump. After the addition was completed, the resulting solution was refluxed for another 8 h. The solvent was then removed under reduced pressure. The residue was refluxed with water (50 mL), filtered, and dried under vacuum for 12 h to give the desired cyclic oligomer **28b**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.98–7.06 (m, 8H, H-d,g), 7.32–7.40 (m, 4H, H-h), 7.55 (d, J = 8.8 Hz, H-c), 7.79 (d, J = 8.8 Hz, H-c). The labeling scheme for the proton assignments can be found in Scheme 5.

***cyclo*-Poly(oxy-1,4-phenylenecarbonyl-1,4-phenyleneoxy-1,4-phenyleneisopropylidene-1,4-phenylene) (28c).** The desired cyclic oligomer **28c** was prepared according to the same procedure as the synthesis of cyclic oligomer **28b**, using difluorobenzophenone (**27**) and BPA (**7c**) as starting materials: ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.70 (s, 6H, Me), 6.95–7.05 (m, 8H, H-d,g), 7.22–7.28 (m, 4H, H-h), 7.71 (d, J = 8.8 Hz, H-c), 7.78 (d, J = 8.8 Hz, H-c); ^{13}C NMR (125 MHz, $CDCl_3$) δ 30.9 (Me), 42.3 (CMe_2), 117.0 (C-d), 119.5 (C-g), 128.3 (C-h), 132.0–132.2 (C-b,c), 146.7–146.9 (C-i), 153.4 (C-f), 161.4 (C-e), 194.2–194.6 (C-a). The labeling scheme for the carbon and proton assignments can be found in Scheme 5.

***cyclo*-Poly(oxy-1,4-phenylenethio-1,4-phenyleneoxy-1,4-phenylenecarbonyl-1,3-phenylenecarbonyl-1,4-phenylene) (30b).** The cyclization reaction was conducted in a 100 mL three-neck round-bottom flask equipped with a nitrogen inlet, thermometer, Dean–Stark trap, and condenser. The flask was charged with 50 mL of DMF, 5 mL of toluene, 4,4′-thiodiphenol (**7b**) (0.5 g, 2.29 mmol), 1,3-bis(4-fluorobenzoyl)benzene (**29**) (0.74 g, 2.29 mmol), and 5 g of potassium carbonate. The solution was magnetically stirred and heated under reflux for 16 h at 145–8 °C. The reaction mixture was filtered immediately when it was still hot. The solvent was then removed from the filtrate under reduced pressure. The residue was dissolved in 10 mL of hot DMF and the desired oligomers precipitated as a white solid in the methanol (50 mL). The precipitate was filtered and dried in a vacuum oven (120 °C) for 12 h. The yield of **30b** was 900 mg (78% yield): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.00–7.08 (m, 8H, H-h,k), 7.34–7.42 (m, 4H, H-l), 7.58–7.68 (m, 1H, H-a), 7.80–7.86 (m, 4H, H-g), 7.96–8.14 (m, 3H, H-b,d). The labeling scheme for the proton assignments can be found in Scheme 6.

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Supporting Information Available: Tables of MALDI-TOF-MS data of compounds **8a**, **8c**, **8d**, **9b**, **9c**, **9d**, **9e**, **9f**, **10b**, **22**, **23a**, **23b**, **23c**, **24c**, **28b**, **28c**, and **30b** (5 pages). Ordering information is given on any current masthead page.

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