Synthesis of Macrocyclic Aryl Ethers Containing the Tetraphenylbenzene Moiety

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ABSTRACT: Cyclic aryl ether ketone oligomers containing the 1,2-dibenzoyl-3,4,5,6-tetraphenylbenzene moiety were synthesized in high yield by reaction of 1,2-bis(4-fluorobenzoyl)-3,4,5,6-tetraphenylbenzene with bisphenols in DMF in the presence of potassium carbonate. The diketone monomer has low solubility in DMF, and high dilution conditions were obtained by adding the solid reactants in portions during the course of the reaction. The cyclic ether ketone oligomers were also transformed into cyclic ether phthalazines by reaction with hydrazine. The cyclics formed are crystalline and have lower T_gs than their amorphous linear counterparts.

Introduction

Macrocyclic oligomers as precursors of high-performance polymers have received a great deal of attention[1−7] since the pioneering work of Brunelle et al. on macrocyclic carbonates.[8−10] Macrocycles can be processed at much lower temperature than the corresponding high molecular weight polymers since they have much lower melt viscosity, and they can undergo controlled ring-opening polymerization without liberation of byproducts. All of these advantages make them potentially applicable in the areas of advanced thermoplastic composites and high-temperature adhesives. We have reported that poly(ether ketone)s containing the *o*-dibenzoylbenzene group are a class of soluble, amorphous, high-performance polymers with high T_gs and excellent mechanical properties.[11] In our laboratory, we have also developed an efficient method for the synthesis of marcocyclic procursors of this class of polymers containing 1,2-dibenzoylbenzene and 1,2-dibenzoyl-3,6-diphenylbenzene moieties using a high-dilution method by slow addition of reactants to the reaction mixture via a syringe pump. The macrocycles formed readily undergo ring opening to give linear high molecular weight polymers.[12,13] Herein we report the synthesis of macrocyclic ethers containing the 1,2-dibenzoyl-3,4,5,6-tetraphenylbenzene moiety. These macrocycles also readily undergo ring-opening polymerization to give linear high molecular weight polymers under conditions which will be reported in a later paper.

Experimental Section

1,2-Bis(4-fluorobenzoyl)-3,4,5,6-tetraphenylbenzene (**1**) was synthesized according to the previously reported method.[11] 4,4′-(1-Methylethylidene)bis(phenol) (BPA), 4,4′-dihydroxybiphenyl, and 9,9′-bis(4-hydroxyphenyl)fluorene were supplied by General Electric Co. 4,4′-(Hexafluoroisopropylidene)diphenol, hydroquinone, bis(4-hydroxyphenyl) sulfone, and 4,4′- thiodiphenol were purchased from Aldrich Chemical Co. and purified by recrystallization. All solvents were used directly as obtained without further purification.

GPC analyses were performed on a Waters 510 HPLC equipped with 5 μm phenogel columns (linear, 3 × 500 Å) arranged in series with chloroform as solvent and UV detector. DSC scans were obtained using a Seiko DSC instrument at a heating rate of 20°C/min in N_2 (160 mL/min). The weight loss data were obtained from a Seiko 220 TG/TGA instrument at a heating rate of 20 °C/min in nitrogen. Gradient HPLCs were performed on a Milton Roy CM4000 multiple solvent delivery system with a C8 Prime Sphere 4.6 × 250 mm column, THF, and water as eluent solvent, and a UV detector at 300 nm. All samples were stirred on a mechanical shaker until dissolved into solutions before analyses. NMR spectra were recorded on a Varian Unity 500 instrument (500 MHz), and $CDCl_3$ was used as solvent. TMS was used as reference for ^{1}H-NMR, and computer reference was used directly for ^{19}F-NMR. For easy identification, fluorobenzene was added.

MALDI−TOF−MS Analysis for the Cyclic Samples. Matrix-assisted laser desorption ionization−time of flight−mass spectroscopy analysis was performed on a KOMPACT-MALDI-TOF-MS instrument. The analysis solution was prepared from 20 μL of cyclic sample solution, 20 μL of silver trifluoroacetate solution, and 100 μL of dithranol solution (matrix). The cyclic sample solution was prepared from 5 mg of sample of 1 mL of chloroform. The matrix solution consisted of 10 mg of dithranol and 1 mL of chloroform. The concentration of silver trifluoroacetate was 5 mg/mL. The sample solution (0.2 μL) was spotted on the sample slot and subjected to analysis. The laser power was selected as 119.

General Procedure to Prepare Macrocyclic Ether Ketones. A 1000 mL three-neck round bottom flask equipped with a Dean−Stark trap and a nitrogen inlet was charged with 500 mL of DMF, 25 g of anhydrous potassium carbonate, and 40 mL of toluene. The mixture was refluxed for 1 h to remove water; then 5.0 g of 1,2-bis(4-fluorobenzoyl)-3,4,5,6-tetraphenylbenzene (**1**) and an equivalent amount of bisphenol were added in 10 portions directly to the flask in solid form over 9 h. The resulting mixture was kept at reflux for another 10 h and cooled down. After filtration, the solvents were removed on a rotary evaporator under vacuum. The resulting solid was dissolved in 250 mL of chloroform and refiltered. The solution was concentrated under vacuum in a rotary evaporator to 50 mL and precipitated out by addition to methanol. The resulting solid was dried at 100 °C for 24 h under vacuum. All the cyclic oligomers were obtained as white powders.

Preparation of Linear Oligomers of 4. A 25 mL three-neck round bottom flask equipped with a Dean−Stark trap and a nitrogen inlet was charged with 1.500 g (2.4 mmol) of **1**, 0.547 g (2.4 mmol) of 4,4′-(1-methylethylidene)bis(phenol), 3.0 g of anhydrous potassium carbonate, 8.0 mL of DMF, and 6.0 mL of toluene. The mixture was placed in a preheated oil bath and kept at reflux for 1 h. After cooling down, the reaction mixture was filtered into a methanol−glacial acetic acid solution to precipitate out the products. The solid products were dissolved in 20 mL of chloroform and filtered through a thin layer of Celite. The chloroform solution was condensed and poured into 100 mL of methanol. The white linear oligomers was obtained by filtration and dried at 100 °C under vacuum for 24 h. Yield: 1.46 g (71%).

General Procedure for the Preparation of Cyclic Ether Phthalazines. To a cooled solution of 0.8 g of the above cyclic ether ketone in dioxane (12 mL) and concentrated

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Table 1. MALDI–TOF–MS Analysis of Cyclic Ether Ketones

		M1 + Ag	M2 + Ag	M3 + Ag	M4 + Ag	M5 + Ag	M6 + Ag	M7 + Ag	M8 + Ag
3a	measd		1737.7	2553.2	3369.6	4185.1	5000	5814	
	calcd		1738	2553	3368	4183	4998	5813	
	intensity		100	93	53	20	7	1	
3b	measd		1653.8	2426.6	3199.8	3973.1	4747	5521.4	6289.4
	calcd		1653.6	2624.4	3199.3	3972.1	4745	5517.8	6290.6
	intensity		92	100	66	42	17	6	2
3d	measd		1793.5	2636.8	3480.3	4322.4	5167.3		
	calcd		1794	2637	3480	4323	5166		
	intensity		100	45	20	7	2		
3e	measd	1002.6[a]	1898	2794.8	3690	4585			
	calcd	1003	1898	2793	3688	4583			
	intensity	61	100	36	10	2			
3f	measd		1982	2919.9	3857.6	4795.2	5733.1	6673.2	
	calcd		1982	2919	3856	4793	5730	6667	
	intensity		100	56	28	10	3	1	
3g	measd		1502.1	2199.4	2897	3594.6	4293	4989.2	
	calcd		1501	2198	2895	3592	4288	4985	
	intensity		50	100	56	25	13	2	
3h	measd		1782	2619.7	3456.6	4293			
	calcd		1782	2619	3456	4292			
	intensity		100	18	4	0.5			
3i	measd		1718.7	2524.2	3329.6	4137.1	4942.1		
	calcd		1718	2523	3328	4132	4937		
	intensity		100	46	21	8	3		

[a] Another molecular peak observed is M1 without silver attachment: measd, 895.6; intensity, 83%; calcd, 895.

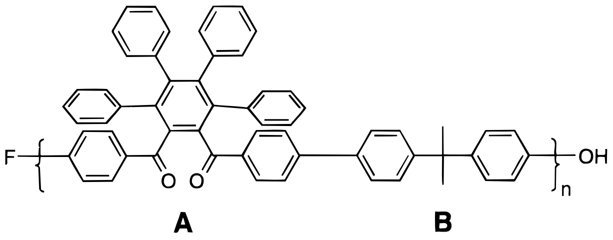
hydrochloric acid (2 mL) was added hydrazine monohydrate (8 mL) over a period of 15 min. The reaction mixture was refluxed for 8 h, cooled down, and poured into 25 mL of water. The light yellow solid was washed several times with methanol and dried at 100 °C for 24 h under vacuum.

Results and Discussion

Cyclic Ether Ketones. We have previously reported the synthesis of macrocyclic oligomers containing the 1,2-dibenzoylbenzene and 1,2-dibenzoyl-3,6-diphenylbenzene moieties under high-dilution conditions by reaction of the corresponding 1,2-bis(4-fluorobenzoyl)benzenes with bisphenols in the presence of potassium carbonate in DMF solution. Ring-opening polymerization results in linear, amorphous polymers with high T_gs and excellent mechanical properties.[12–15] Polymers containing the tetraphenylbenzene moiety are also amorphous and soluble in a variety of solvents and have significantly higher T_gs.[11,16] The corresponding macrocycles could not be easily prepared by the previously described method by addition of the reactions slowly to the reaction mixture via a syringe pump because the starting material, 1,2-bis(4-fluorobenzoyl)-3,4,5,6-tetraphenylbenzene (**1**), has low solubility in DMF, which is the preferred solvent for the reaction, at room temperature.[12] We were successful in achieveing high-dilution reaction conditions by adding the reactants, 1,2-bis(4-fluorobenzoyl)-3,4,5,6-tetraphenylbenzene and bisphenol, in portions in solid form to the reaction mixture. The reactants were delivered in 10 portions over 9 h. This strategy gave us very high yields of cyclic ether ketones containing the tetraphenylbenzene moiety (Table 1). The reaction is shown in Scheme 1. If all the reactants were added to the reaction mixture in one portion, significant amounts of high molecular weight linear oligomers were obtained (Figure 1B and 2B). The lower yields of **3b**,**g** (Table 2) are due to the lower solubilities of their dimers in DMF, some of which were lost during workup. However, the low yield of **3h** can be attributed to the low reactivity of bis(4-hydroxyphenyl) sulfone in the nucleophilic displacement reaction. Electronegative sulfone groups significantly lower the reactivity of the phenoxide anion.

GPC and gradient HPLC methods were used to analyze the products. All of them showed that the major products were cyclic dimer, trimer, and tetramer. Only small amounts of higher oligomers were formed. GPC results for macrocycle **3a** are shown in Figure 1. **3a** has a number-average molecular weight of 2500 and a weight-average molecular weight of 5200 calibrated against polystyrene standards. Analysis by gradient HPLC gave similar results. The gradient conditions were as follows: at 0 min, THF 70%, H_2O 30%; at 20 min, THF 90%, H_2O 10%; at 22 min, THF 100%; at 25 min, THF 100%; at 27 min, THF 70%, H_2O 30%; at 30 min (end), THF 70%, H_2O 30%. Generally, cyclic ether ketones made by this method consist of around 35% dimer, 20% trimer, 12% tetramer, and 7% pentamer.

To be convinced the products we obtained were cyclic oligomers, an authentic linear oligomer sample, **4**, was synthesized and comparison studies were made between linear oligomer **4** and the corresponding cyclic oligomer **3a**. The linear oligomers were synthesized according to typical polymerization conditions by stopping the reaction at an early stage. The number-average molecular weight of this linear oligomer sample is 3200, and the weight-average molecular weight is 4300, analyzed by GPC, which are comparable to those of cyclic oligomer **3a** (Figure 1). It is anticipated that three types of linear oligomers are possible: **A**(**BA**)$_{n-1}$**B**, (**BA**)$_{n-1}$**B**, **A**(**BA**)$_{n-1}$**BA**. Gradient HPLC analysis shows such a distribution pattern (Figure 2C). Gradient HPLC data were also obtained for the mixture of equivalent amounts of cyclic oligomer **3a** and linear oligomer **4** (Figure 2D). These HPLC profiles shown in Figure 2 indicate that linear oligomers can be easily detected under the present gradient HPLC conditions. Since the gradient



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Scheme 1. Preparation of Cyclic Ketone Ethers Containing the Tetraphenylbenzene Moiety

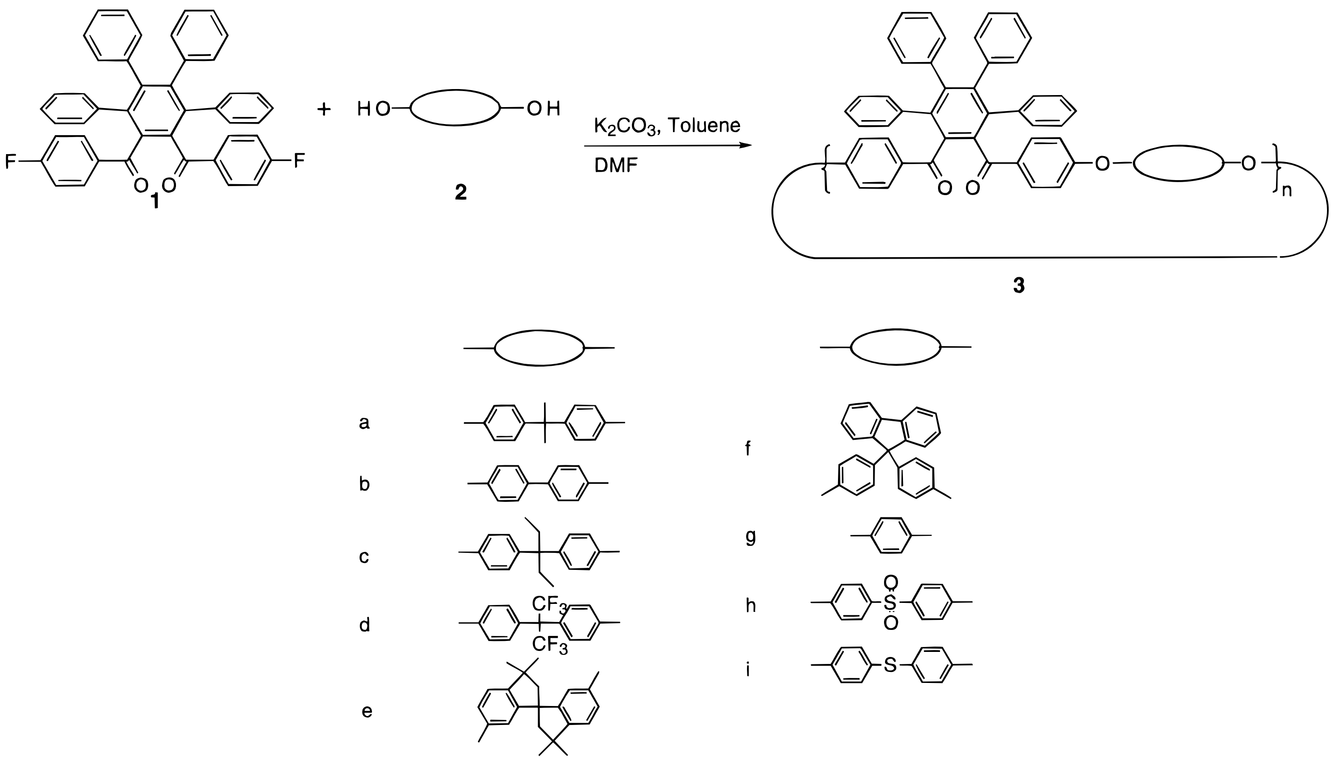


Table 2. Properties of Cyclic Ether Ketones Containing the Tetraphenylbenzene Moiety

cyclics	yield (%)^a	$M_n{}^b$	$M_w{}^b$	T_g (°C)^c	T_m (°C)^c	TGA (°G)^d
3a	70	2500	5200	243 (265)^e	469	521
3b	64.1	2500	7000	267 (292)^e		487
3c	84	2200	4300	251		461
3d	85.1	1900	3300	254 (278)^e	394	507
3e	85	800	1100	379	430	467
3f	85	2000	3600	296 (313)^e	425	460
3g	65	2200	3700	260 (273)^e	354	457
3h	55	1600	2300	257		443
3i	90	2400	4800	236	377	466

[a] Isolated yield. [b] Measured by GPC and calibrated against polystyrene. [c] Measured under N_2 by DSC; heating rate was 20 °C/min. [d] Temperature at which 5% weight loss was observed under N_2 atmosphere; heating rate was 20 °C/min. [e] T_g of corresponding polymer.

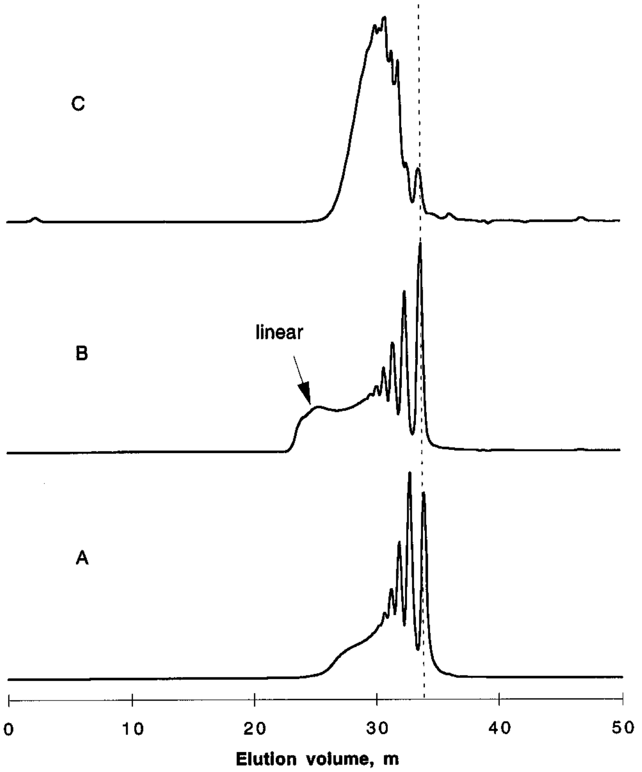


Figure 1. GPC charts. A: Cyclic oligomer **3a** obtained by adding reactants in 10 portions. B: Cyclic oligomer **3a** obtained by adding reactants in one portion. C: Linear oligomer **4**.

HPLC of the cyclic oligomers shows no evidence of linear oligomers, one can conclude that these cyclic oligomers are clean.

^{1}H- and ^{19}F-NMR spectra were taken for all the samples, and no hydroxy and/or fluoro end groups were detected by these studies, although these end groups are easily detected for the linear oligomers. A comparison of ^{19}F-NMR between linear oligomer **4** and cyclic oligomer **3a** is shown in Figure 3. NMR studies provided additional support for the cyclic nature of the structures obtained by the present method.

The most powerful tool for analysis of the cyclics is MALDI–TOF–MS. Dithranol was chosen as the matrix for the analysis. Without the addition of a silver compound as a cationization agent, the mass spectra were not clean and difficult to interpret. Even with addition of sodium salt, the spectra were still difficult to interpret. However, when a silver salt was added, the mass spectra were much cleaner. Generally, we can see macrocyclics with repeating units up to 8 or 9 units. The MALDI–TOF–MS of cyclic oligomer **3a** is shown in Figure 4. The perfect match of measured mass with the calculated mass of cyclics (Table 1) also confirmed the cyclic structures. In Table 1, peak intensities are reported relative to the strongest molecular peak. Comparing Figure 2 with Figure 5, we can see that MADLI–TOF–MS gives almost the same distribution pattern as gradient HPLC. However, for composition analysis of cyclics, gradient HPLC is much preferred. The MALDI–TOF–MS of linear oligomer **4** is shown

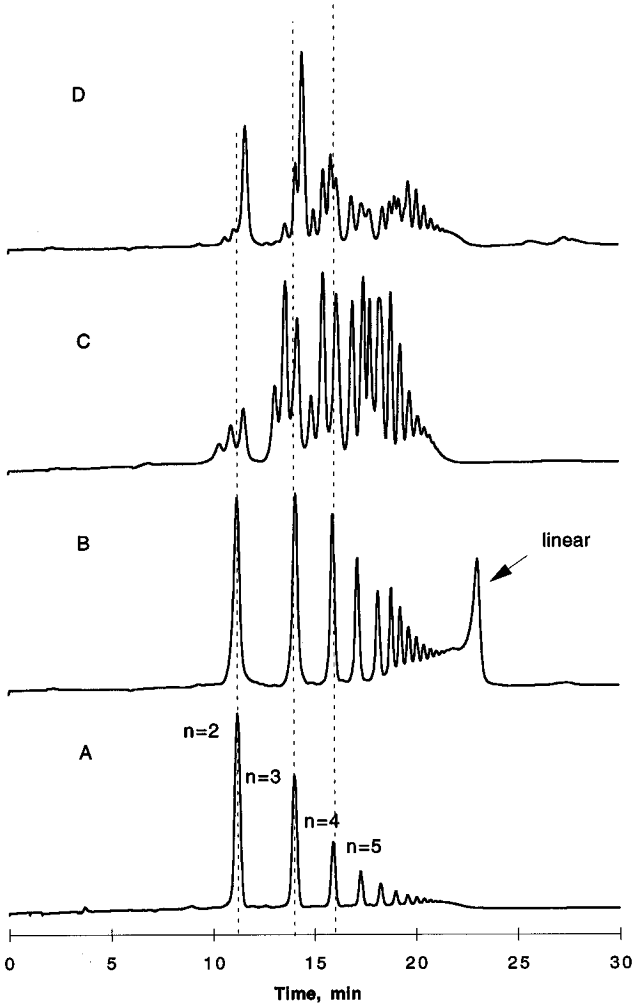


Figure 2. Gradient HPLC charts. A: Cyclic oligomer **3a** obtained by adding reactants in 10 portions. B: Cyclic oligomer **3a** obtained by adding reactants in one portion. C: Linear oligomer **4**. D: Mixture of equivalent amounts of cyclic oligomer **3a** and linear oligomer **4**.

in Figure 5. In this spectrum, three different kinds of linear oligomer peaks are clearly and unambiguously shown, as is also suggested by gradient HPLC. This spectrum also indicates that the linear oligomers contain small amounts of cyclic dimer and trimer. By comparing Figures 4 and 5, one can easily draw the conclusion that the oligomers obtained by the present method are cyclics.

The X-ray structure of the cyclic dimer obtained by reaction of 1,2-bis(4-fluorobenzoyl)benzene and 4,4′-thiobiphenol has been resolved.[17] The ease of formation of cyclics is attributed to the conformation of the diketone reactant. This can be seen from the molecular model of 1,2-bis(4-fluorobenzoyl)-3,4,5,6-tetraphenylbenzene, shown in Figure 6, which was generated by a molecular mechanics calculation using the CAChe program on a Macintosh computer. The two fluoro atoms are in bent positions which facilitate the formation of cyclics. In the case of **3e**, due to this bent conformation and, in addition, the bent conformation of the bisphenol spiro[biindanebisphenol] (SBI), the cyclic monomer was the predominant product. This behavior is quite different from other cyclics in this series. The use of monomers such as SBI to facilitate the formation of cyclics has also been reported by other researchers.[6,10,18]

As expected, all of the cyclic ether ketones show T_gs >230 °C. The T_gs of the macrocyclic oligomers are generally 13−25 °C lower than the linear analogs. The thermal properties of these cyclics are summarized in Table 2. The strong endothermic peaks of these cyclics correspond to melting points due to the high percentage of dimers and trimers which they contain. Although the melting points of these cyclics are very high, they readily flow above their T_ms. The very high T_ms of these cyclics would require the use of very high temperatures during the ring-opening polymerization reactions; however, when two or three of these cyclics are mixed together, they have much lower melting points (around 300 °C). Therefore, ring-opening polymerization can be easily

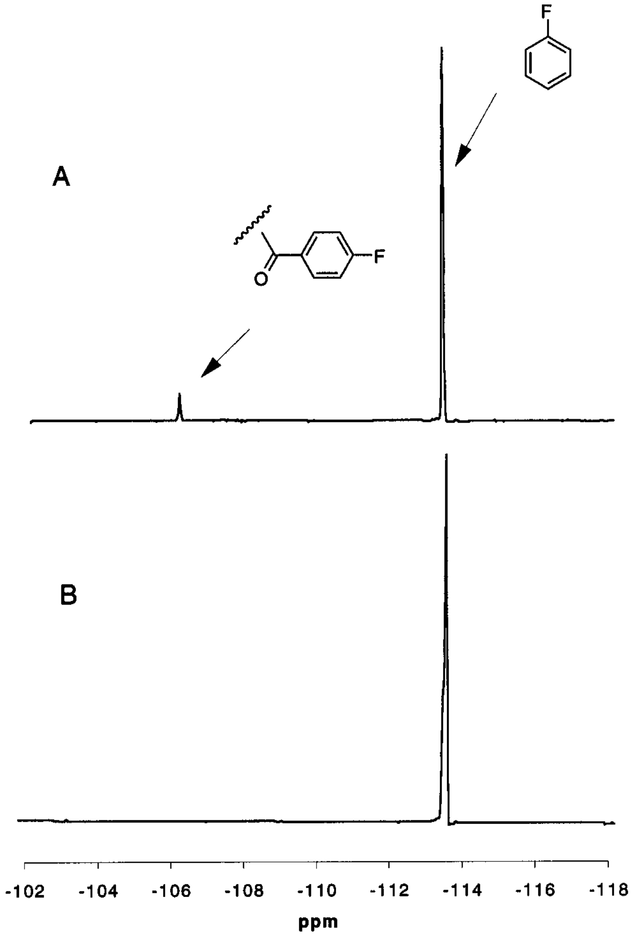


Figure 3. ^{19}F-NMR of cyclic oligomer **3a** and linear oligomer **4**. A: Linear oligomers. B: Cyclic oligomers.

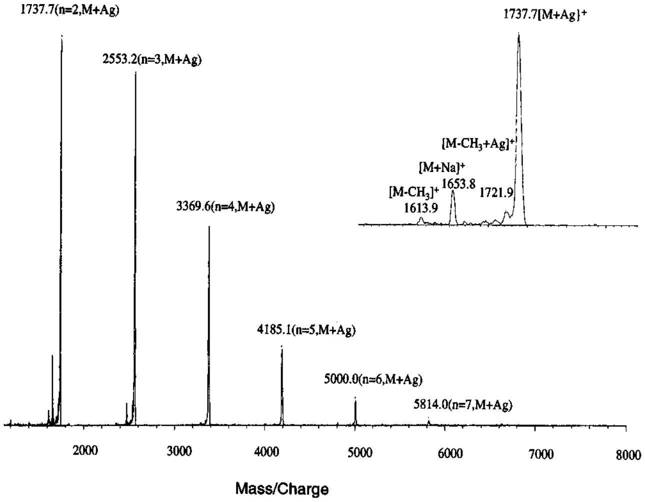


Figure 4. MALDI−TOF−MS of cyclic oligomer **3a**.

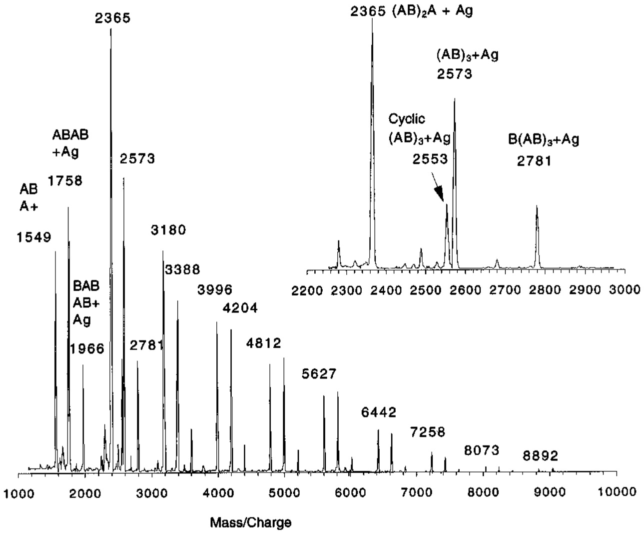


Figure 5. MALDI−TOF−MS of linear oligomer **4**. A: tetraphenyl diketone moiety. B: BPA moiety.

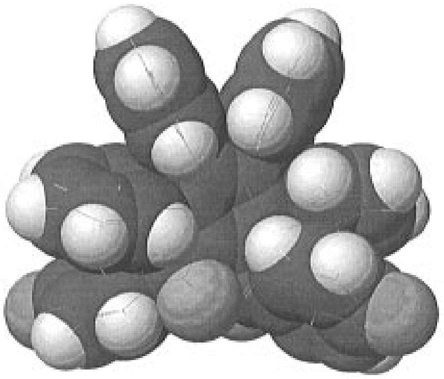
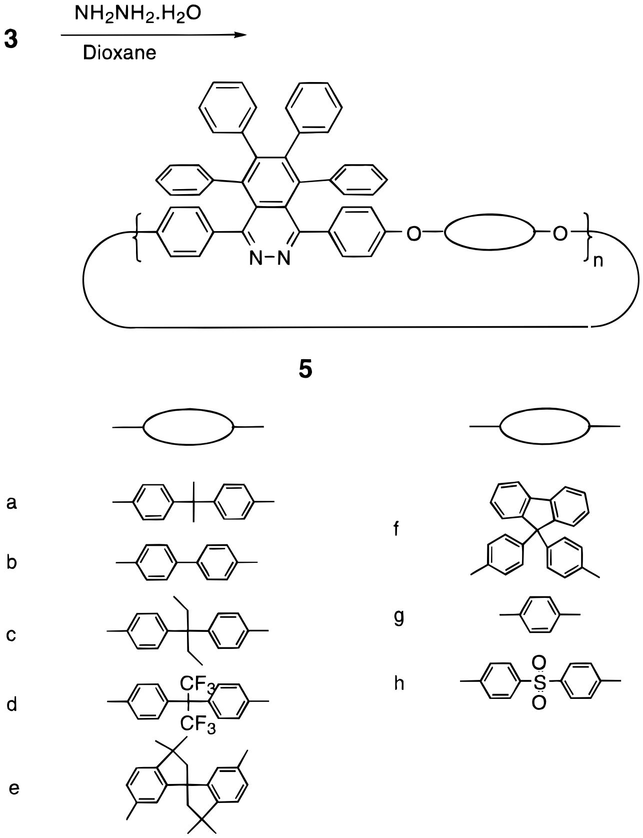


Figure 6. Stable conformation of 1,2-bis(4-fluorobenzoyl)-3,4,5,6-tetraphenylbenzene.

carried out around 350 °C. The details of the ring-opening polymerization will be reported in a later paper.

Cyclic Ether Phthalazines. The cyclic ether ketones have also been transformed into cyclic ether phthalazines which in the corresponding linear polymers have higher T_gs than the cyclic ether ketones.[16] The reaction is shown in Scheme 2. The completion of the reactions was confirmed by ^{13}C-NMR studies. The ^{13}C peak of the carbonyl group in the starting cyclic was below the detection limit. MALDI−TOF−MS analyses of these cyclic ether phthalazines are quite different from the cyclic ether ketones. The addition of a silver salt does not improve the analysis sensitivity and quality. All of the MS analyses can be carried out without the assistance of silver in the presence of dithranol as matrix, and the results are in agreement with calculated results (Table 3). Samples analyzed in the presence of silver give the same results.

Scheme 2. Conversion of Cyclic Ether Ketones into Cyclic Ether Phthalazines



Model reactions on phthalazines have previously indicated that both rearrangement and cross-linking

Table 3. MALDI−TOF−MS Analysis of Cyclic Ether Phthalazines

		M2	M3	M4	M5	M6	M7	M8
5a	measd	1621	2432.1	3244.7	4056.1	4868.6	5676.5	6490.5
	calcd	1622	2433	3244	4055	4866	5677	6488
	intensity	74.5	100	87	45	16	4	0.5
5b	measd	1539.1	2305.6	3076.4	3846	4616.4	5385.4	6149.7
	calcd	1538	2306	3075	3844	4613	5382	6151
	intensity	85	100	41	50	30	12	3
5c	measd	1671.4[a]	2516.8[a]	3356.9[a]	4197.7[a]	5036[a]	5874.6[a]	6714.6[a]
	calcd	1686	2529	3372	4214	5058	5901	6744
	intensity	65	71	100	59	20	6	2
5e	measd	1782.1	2675.2	3567.9	4458.7	5352		
	calcd	1782	2673	3564	4455	5346		
	intensity	100	24	17	6	0.5		
5f	measd	1865.8	2800.8	3735.6	4671.8	5602.3	6537.1	7481.4
	calcd	1867	2801	3735	4669	5602	6536	7470
	intensity	95	100	71	27	8	2	0.3
5g	measd	1386.8	2077.7	2771.1	3465.6	4159.4	4852.2	5545.5
	calcd	1386	2078	2771	3464	4157	4849	5542
	intensity	32	100	83	92	62	10	5
5h	measd	1665.2	2449.8	3355.7	4188.8	5024.6	5860.4	
	calcd	1666	2499	3332	4165	4997	5830	
	intensity	100	47	41	24	6	0.3	

[a] Molecular peak corresponding to loss of one methyl group.

Scheme 3. Rearrangement Reaction of a Phthalazine

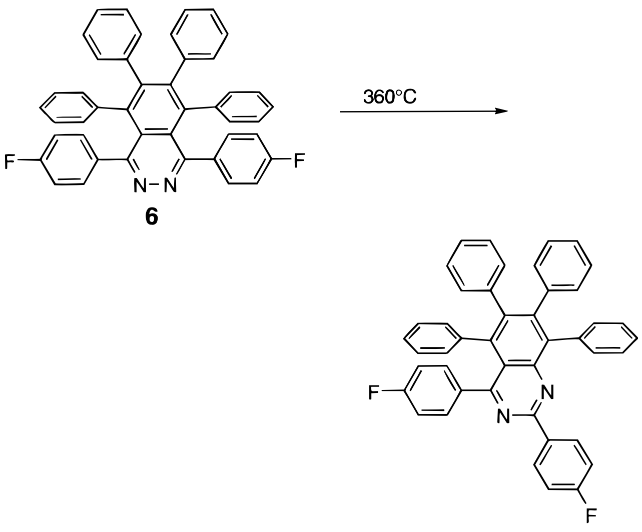


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Table 4. Properties of Cyclic Ether Phthalazines

cyclics	T_{R} (°C)[a]	TGA (°C)[b]	cyclics	T_{R} (°C)[a]	TGA (°C)[b]
5a	330	520	**5e**	331	453
5b	342	550	**5f**	358	543
5c	307	480	**5g**	343	530
5d	332	518	**5h**	319	494

reactions have occurred on heating.[19] The rearrangement reaction on phthalazine **6** forms a quinazoline, **7** (Scheme 3); however, the nature of the cross-linking reaction is unclear. DSC studies have shown that in this class of cyclics some exothermic reactions take place when heated higher than 300 °C. As expected, the DSC scan of **5b** shows similar behavior. Generally, these reactions take place around 330 °C (Table 4). These reactions precluded further work on the ring-opening polymerization of these cyclics because melting points of this class of cyclics are >330 °C and polymerization has to be carried out above the melting points which would be above the decomposition temperature.

Conclusions

A new series of macrocyclic ether ketones containing the tetraphenylbenzene moiety has been synthesized by a high-dilution method. To overcome the problem of solubility of the diketone reactant, the reactants were added in solid form over a period of several hours. This synthetic strategy gave high yields of macrocyclic ether ketones consisting principally of dimer, trimer, and tetramer. This series of cyclics shows high thermal stabilities, and they have high T_{g}s. The macrocyclic oligomers have extremely high melting points; however, by the use of mixtures of cyclics, the T_{m}s are significantly lowered to make them suitable precursors for ring-opening polymerization to give high-performance polymers. Cyclic ether ketones were also transformed into ether phthalazines which undergo exothermic reactions around 330 °C which precludes their use in ring-opening polymerization reactions.

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