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Convenient Synthesis and Facile Polymerization of Cyclic Aryl Ether Ketones Containing the 1,2-Dibenzoylbenzene Moiety

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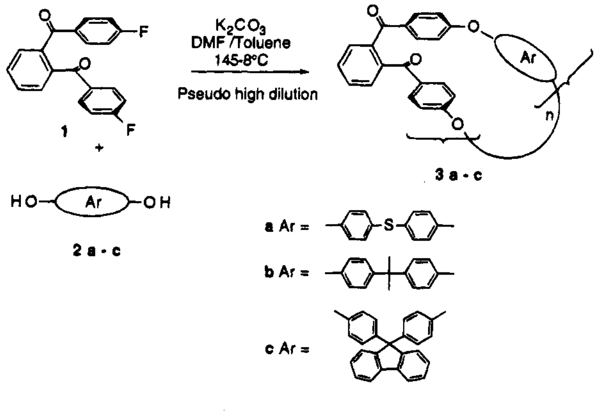
Introduction. Poly(ether sulfone)s and poly(ether ketone)s are high-performance thermoplastics with high thermooxidative stability and T_g. In recent years, the advantages of using cyclic aryl ethers as precursors of high-performance thermoplastics has been well recognized.[1-5] The unique combination of low melt viscosity of cyclic oligomers together with the possibility of undergoing controlled polymerization in the melt without the liberation of volatile byproducts makes them potentially applicable in the areas of advanced thermoplastic composites and high-temperature adhesives.

Up to now no convenient and high-yield synthesis for cyclic aryl ether oligomers has been available,[1,3,5] and studies of their polymerization and physical behavior are rather scarce in the literature.

Herein, we disclose an efficient synthesis of cyclic aryl ether oligomers which proceeds in high yield. Furthermore, these oligomers undergo melt polymerization readily, in the presence of anionic catalyst, to give high T_g (up to 240 °C) and high molecular weight polymers. In addition, we report the use of matrix-assisted laser desorption ionization mass spectrometry (MALDI)-MS, which enables the detection of oligomers with mass up to 5000 Da. This technique, in addition to NMR and GPC, is shown to be a very powerful tool for the analysis and proof of the cyclic nature of the oligomers.

Results and Discussion. Synthesis. We have found that a high yield of cyclic aryl ether ketones can be prepared from 1,2-bis(4-fluorobenzoyl)benzene (**1**)[6] by reaction with a number of bisphenols (eq 1 and Table 1). A pseudo-high-dilution method was used to achieve a high yield of cyclic oligomers.[7] 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.[8] Following the addition of reactants, it takes another 8 h of reflux to ensure complete reaction.



(1)

Table 1. Yields and Properties of Cyclic Oligomers 3a–c

Ar	yield[a]/%	M_n[b]	M_w[b]	T_g[c]/°C	T_m[c]/°C	TGA[d]/°C
3a	90	1300	3100	142 (156)[e]	234	476
3b	95	1500	4800	157 (180)[e]	324	452
3c	80	1700	5100	220 (240)[e]	ND[f]	517

[a] Isolated yield. [b] Measured by GPC and calibrated against polystyrene standards, unit in g/mol. [c] Measured by DSC under a nitrogen atmosphere (50 mL/min); heating rate was 20 °C/min. [d] Reported 5% weight loss under a nitrogen atmosphere (200 mL/min); heating rate was 20 °C/min. [e] T_g of the corresponding linear polymer. [f] ND = not detected.

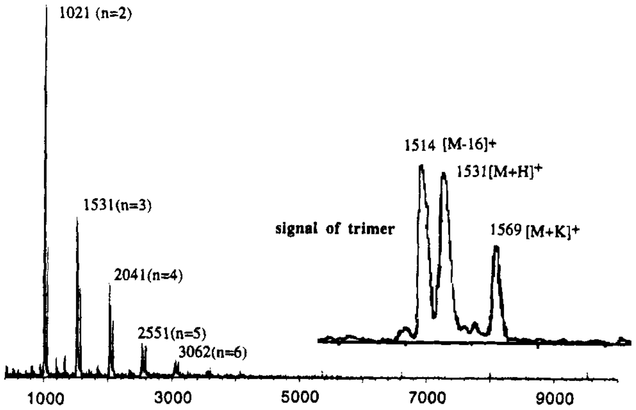
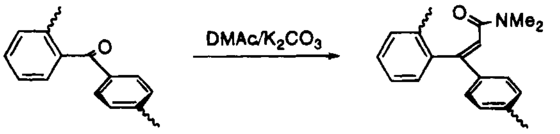


Figure 1. MALDI-MS of **3b**.

DMF has been demonstrated to be the best solvent for formation of cyclic oligomers. *N,N*-Dimethylacetamide (DMAc), *N*-methyl-2-pyrrolidinone (NMP), and dimethyl sulfoxide (DMSO) all failed to give a clean reaction. Based on ^{1}H NMR and MS analysis, we suspect undesirable side reactions may have occurred between these solvents and the reactants or the oligomers formed. We find that when DMAc is used an aldol condensation reaction takes place between the acidic α-methyl group of DMAc and the carbonyl groups of monomer **1** and oligomers form (eq 2). We suspect that this side reaction may also happen with NMP or DMSO.



(2)

We generally employ K_2CO_3 as base; however, we find that using Cs_2CO_3 as base reduced the reaction time by half, from a total of 16 h to 8 h. Cesium phenoxide has been shown to have a higher reactivity than potassium phenoxide in these displacement reactions.[9]

Characterization. The reaction generates a mixture of oligomeric cyclic aryl ether ketones. Analysis based on GPC, HPLC, and MALDI-MS indicates that the range of oligomerization is principally from degree of polymerization of 2 up to 10. A typical mixture contains 37% cyclic dimer, 16% trimer, 10% tetramer, 6% pentamer, 4% hexamer, and 25% higher homologues. A MALDI-MS (Figure 1) and a GPC trace (Figure 2) of **3b** are shown. MS of **3b** (Figure 1) reveals cyclic oligomers up to hexamer ($n = 6$) with reasonable signal to noise ratio. The expanded scale of the MS spectrum of **3b** (Figure 1) shows three signals for each oligomer. For example, signals for the trimer are located at 1514, 1531, and 1569 Da. The signal at 1531 Da corresponds

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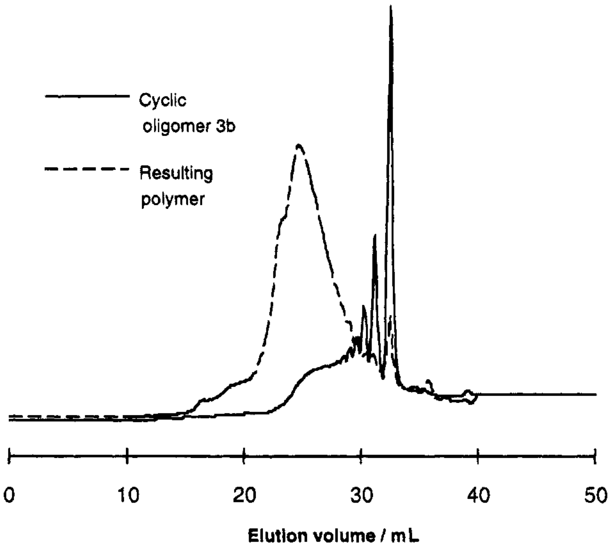
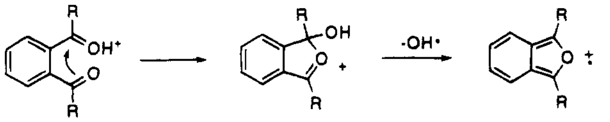


Figure 2. GPC traces of oligomer **3b** and polymerization product of **3b**.

to the protonated molecular ion peak, that at 1569 Da is due to the adduct of the trimer with a potassium cation, while the signal at 1514 Da is due to the intramolecular cyclization of the trimer of **3a** to form isobenzofuran (eq 3).



(3)

Thermal analysis shows that cyclic oligomers **3a** and **3b** exhibit a moderate T_m endotherm along with T_g (Table 1). Surprisingly, a T_m is not observed for sample **3c**.

^{13}C NMR studies of the mixture indicate that phenolic end groups, if present, are below the detection limit, and ^{19}F NMR studies indicate that there is one fluorophenyl end group for every 200 repeating units. Therefore, the present procedure produces a mixture of cyclic oligomers in high yield with negligible amount of linear oligomers. They are readily soluble in chloroform.

Polymerization. Ring-opening polymerization (ROP) of the cyclic oligomers prepared can be initiated through an ether exchange reaction. Since the aryl ether linkage is activated by an electron-withdrawing group, it will undergo ether exchange reaction readily.[10] Therefore, melt polymerization has been performed on the cyclic oligomers **3a** and **3b** with 1 mol % of CsF as catalyst. Both oligomers undergo facile polymerization within 30 min at 300 and 340 °C, respectively, to give high molecular weight polymers. Cyclic oligomer **3a** gave polymer with M_w = 510 000 and M_n = 18 000, and **3b** gave polymer with M_w = 165 000 and M_n = 10 000. A GPC trace for the polymer from **3b** is shown in Figure 2.

We find that polymerization using CsF results in a polymer with a broad molecular weight distribution containing an extremely high molecular weight fraction, up to a million, based on GPC analysis. When polymerization was performed at higher temperature and longer time, the polymer had an extremely high M_w and was insoluble in chloroform. We suspect that the wide molecular weight distribution may have resulted from a branching side reaction, which resulted in the formation of an extremely high molecular weight fraction. Furthermore, the broad distribution can also be attributed to the presence of an equilibrium amount of cyclic oligomers which remains as a result of a ring–chain equilibrium. Interestingly, we find that potassium carbonate is a very efficient catalyst for polymerization of cyclic oligomers **3a**. Preliminary studies indicate that it is twice as efficient as CsF.

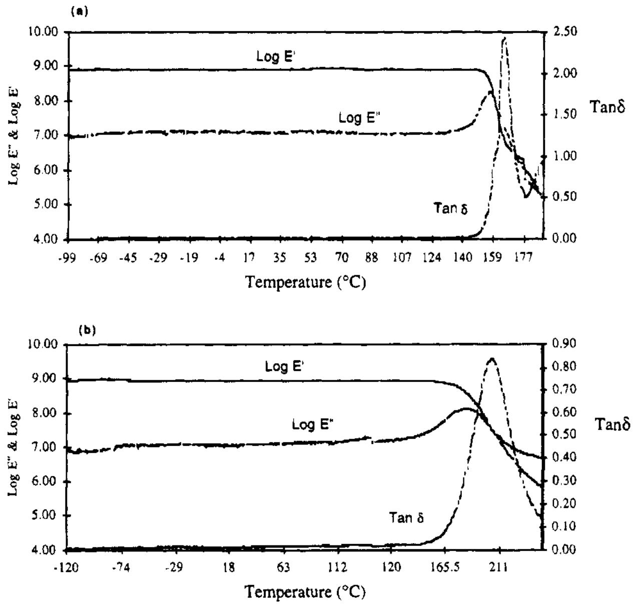


Figure 3. DMTA spectra of polymer (a) from **3a** and (b) from **3b**.

Cyclic oligomers **3a** and **3b** mixed with 1 mol % of CsF have been compression molded at moderate temperature and polymerized *in situ* into rectangular bars. Preliminary dynamic mechanical thermal analysis results (Figure 3) show that the stiffness of both materials is maintained up to their T_gs. Polymer **3a** shows a much sharper glass transition and higher value of mechanical damping, which indicates this polymer should have a much higher toughness.

Experimental Section. General Procedures. 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 a UV detector. Dynamic mechanical property measurements were performed on a Polymer Laboratories dynamic mechanical thermal analyzer (DMTA) in the dual-cantilever bending mode at a frequency of 1 Hz under a nitrogen atmosphere. Storage moduli (E'), loss moduli (E''), and loss tangents (tan δ) were obtained as a function of temperature at a heating rate of 2 °C/min.

Synthesis of 3a. The cyclization reaction was conducted in a 3 L three-neck round-bottom flask which was 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 145–148 °C. A solution of 4,4'-thiodiphenol (**2a**) (16.26 g, 74 mmol) and 1,2-bis(4-fluorobenzoyl)benzene (**1**) (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 at 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 **3a** was 34 g (90% yield). A similar procedure was applied for the preparation of **3b** and **3c**.

Molding of Cyclic Oligomers. The cyclic mixed with 1 mol % of CsF, in powder form, was compression molded into rectangular bars at 340 °C under nitrogen for 30 min, the optimum conditions for completion of the ring-opening polymerization.

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