Synthesis of Macrocyclic Arylene Ketone Oligomers Containing the Phthaloyl Moiety by Friedel–Crafts Acylation Reaction

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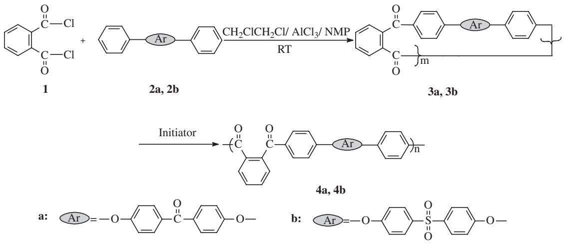
Two kinds of macrocyclic arylene ketone oligomers have been synthesized in high yield from phthaloyl dichloride and various bridge-linking electron-rich aromatic hydrocarbons via the modified Friedel–Crafts acylation reaction. The presence of a Lewis base in this reaction is demonstrated to be advantageous for forming macrocycle oligomers. These resultant oligomers can undergo melt ring-opening polymerization to give polymers with high T_g and excellent thermal stability.

Aromatic poly(ether ketone)s constitute an important family of materials that are currently attracting technical interest on their impressive thermal and mechanical properties and chemical resistance.[1] The advantage of using cyclic aromatic ethers as precursors to prepare these high performance polymers has been recognized for many years. 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, which makes them candidates in the areas of advanced thermoplastic compositions.[2,3] However, up to now, the synthesis of cyclic(aryl ether ketone) oligomers is mainly via the route of nucleophilic aromatic displacement.[3] As another important way for synthesis linear poly(arylene ether ketone)s, the Friedel–Crafts acylation used for synthesis of macrocycles has only been reported by Gibson. The potential advantages of this route for synthesis of macrocycles, such as low cost, mild reaction conditions have been proved, although the cyclization yield was quite low.[4] Herein, we disclose an efficient synthesis of cyclic arylene ketone oligomers in the presence of Lewis base via the Friedel–Crafts acylation reaction.



Scheme 1.

In this work, under pseudo-high dilution conditions, macrocyclic oligomers were synthesized in high yield from *o*-phthaloyl dichloride and bridge-linking electron-rich aromatic hydrocarbons which were prepared from the condensation of phenol with dichloro-monomers (Scheme 1). The pseudo-high dilution conditions were achieved by slowly adding the solution of the two reactants (**1** and **2a**) over 8 h from a dropping funnel to a large amount of solvent containing catalyst. At first, according to Gibson's work, anhydrous aluminum chloride (excess 30–40 mol %) was used as the catalyst in this electrophilic reaction at room temperature. When using dilute HCl to end the reaction, there was a small quantity of linear polymer which could not be dissolved in 1,2-dichloroethane. The crude mixture was analysed by MALDI MS (Figure 1a); the product was complex, although the main product was macrocyclic oligomers. During the reaction, precipitation was observed. The precipitatate was due to linear oligomers and prevented further reaction. It's known that, for the synthesis of high molecular weight linear PAEK by electrophilic reaction, in order to avoid the problem, good results can be achieved by using a mixture composed of catalyst and a Lewis base in a chlorinated organic solvent.[5] When the Lewis base such as *N*-methyl-2-pyrrolidone (NMP) was added to the solvent containing aluminum chloride before the reaction,[6] the product was completely dissolved in the solvent after the reaction was ended by dilute HCl. The MALDI MS of the product is shown in Figure 1b. It's obvious that the reaction mixture consists almost completely of macrocyclic oligomers. The MS spectrum reveals cyclic oligomers from dimer ($n = 2$, $m/z = 993.3$) up to hexamer ($n = 6$, $m/z = 2977.5$), with reasonable signal to noise ratio and shows two signals for each oligomer. For example, the signals for cyclic dimer are located at 993.3 and 976.8 Da. The signal at 993.3 Da corresponds to the protonated

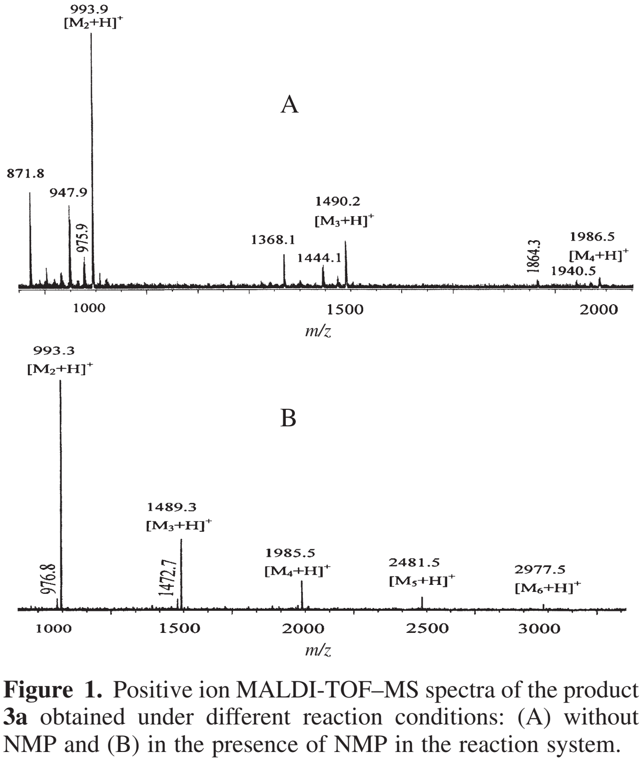


Figure 1. Positive ion MALDI-TOF–MS spectra of the product **3a** obtained under different reaction conditions: (A) without NMP and (B) in the presence of NMP in the reaction system.

molecular ion peak; that at 976.8 Da is due to the intramolecular cyclization of the dimer to form isobenzofuran.

It's well known that the linear oligomers act as chain-transfer agents in the ring-opening polymerization of cyclic oligomers, which is disadvantageous for producing polymer with high molecular weight. It was difficult to separate the linear oligomers and the cyclic oligomers via convenient methods. Therefore, the use of the product prepared from the Friedel–Crafts acylation reaction without Lewis base was limited in ring-opening polymerization because of too much linear oligomers. The selective synthesis of the cyclic oligomers via the Friedel–Crafts acylation can be realized in the presence of Lewis bases, which makes this route significant for synthesizing macrocyclic oligomers. The reaction process of the Friedel–Crafts electrophilic acylation cyclization is altered in the presence of a Lewis base. Although the function of the Lewis base is not completely understood, it appears to maintain the linear oligomers in solution or in a reactive gel state.[5]

Under the condition of using a mixture composed of catalyst $AlCl_3$ (in excess) and NMP in 1,2-dichloroethane, we ran the electrophilic reaction of phthaloyl dichloride with monomer **2b**. The isolated yield of the product was 90%. The MALDI MS of the product give the molecular ion signal for proton adducts of the desired macrocyclic oligomers with excellent signals to noise ratio (Figure 2). GPC analysis indicates that the average degree of polymerization is about 3. The absence of end groups detected by NMR supports the formation of cyclic oligomers, too.[6] According to the signals in the ^{1}H NMR spectrum, it should be pointed out that the acylation reaction took place exclusively at the para position of the ether linkage in electron-rich monomer. From the above analysis, the conclusion can be drawn that the macrocyclic oligomers have been prepared selectively in high yield via electrophilic reaction.

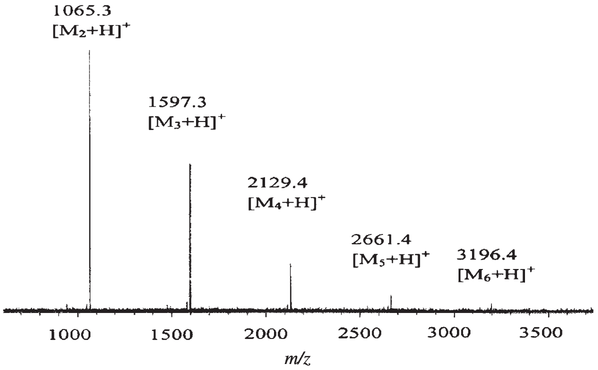


Figure 2. MALDI-TOF–MS spectra of cyclic oligomers **3b**; The data were acquired in the reflection mode using 1,8,9-anthracenetriol as matrix.

Thermal analyses show that the cyclic oligomers have T_gs at 194 °C for **3a** and at 175 °C for **3b** and there is no melting endotherm detected for cyclic oligomers up to 450 °C, which indicated that these cyclic oligomers were amorphous materials. The cyclic oligomers **3a** and **3b** begin to soften near 300 °C and form a clear, homogeneous melt near 320 °C. These cyclic oligomers have low melt viscosities. The melt viscosities of cyclic oligomers **3a**, **3b** are about 2.5 Pa·S and remain stable during the test period.[7] This suggests that the cyclic oligomers **3a**, **3b** are thermally stable at melt temperature under N_2.

The cyclic oligomers can be converted to high molecular weight linear polymer through ring-opening polymerization. Melt polymerizations have been performed on cyclic oligomers **3a** and **3b** with 1.0 mol % potassium 4,4′-biphenoxide as the nucleophilic initiator. Both cyclic oligomers underwent facile polymerization within 40 min at 330 and 340 °C, respectively, to give high molecular weight polymers. About 60% of the polymers **4a** and **4b** prepared via ring-opening polymerization is soluble in DMF and the soluble fractions in DMF has reduced viscosities of 0.42 and 0.36 dL/g, respectively (0.5% solution of DMF at 25 ± 0.1 °C). The insolubility of both polymers probably resulted from branching side reactions occurring at the high reaction temperatures employed. Both polymers, like their cyclic oligomers, are amorphous by DSC , showing a glass transition (onset) at 215.9 °C for polymer **4a** and at 224.2 °C for polymer **4b**. Polymer **4a** has a 5% weight loss at 510 °C, polymer **4b** at 492 °C, under a nitrogen atmosphere.

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6 Preparation of macrocyclic arylene ketone oligomers: The cyclization reaction was conducted in a 500 mL four-neck round bottom flask equipped with a nitrogen inlet and outlet and charged with 250 mL 1,2-dichloroethane and 4.0 g of aluminum chloride. After adding 0.5 mL *N*-methyl-2-pyrrolidone (NMP) dropwise to the stirred flask, a solution of **1** (1.0151 g, 5.0 mmol) and **2b** (2.0119 g, 5.0 mmol) in 50 mL 1,2-dichloroethane was delivered into the mechanically stirred flask over a period of 8 h under dry nitrogen at room temperature. After the addition, the mixture was stirred for another 2 h to ensure complete reaction. Dilute HCl (50 mL) was added slowly to end the reaction. The organic phase was separated and extracted with distilled water three times, evaporated to 10 mL and then poured into 50 mL methanol to precipitate the oligomers. The isolated yield of cyclic oligomers of **3b** was 2.40 g. Cyclic oligomers **3b**, Yield: 90%. ^{1}H NMR (DMSO-d_6): δ 7.86–7.97 (m, 3H), 7.66–7.72 (m, 1H), 7,35–7.44 (m, 2H), 7.06–7.20 (m, 4H); GPC: Mn = 700, Mw = 1000 (against polystyrene standard). Cyclic oligomers **3a**,Yield: 88%. ^{1}H NMR (DMSO-d_6): δ 7.85–8.02 (m, 1H), 7.65–7.82 (m, 3H), 7,40–7.45 (m, 2H), 7.05–7.20 (m, 4H); GPC: Mn = 900, Mw = 2200 (against polystyrene standard).

7 Rheological measurments were performed using a MCR 300 type rheometer with 25 mm parallel plates at a constant shear rate of 0.05 rad/s under N_2 by the rotation test methods.

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