# Communications to the Editor

## Novel Macrocycle by Friedel−Crafts Acylation Cyclization

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*Received March 12, 1996*

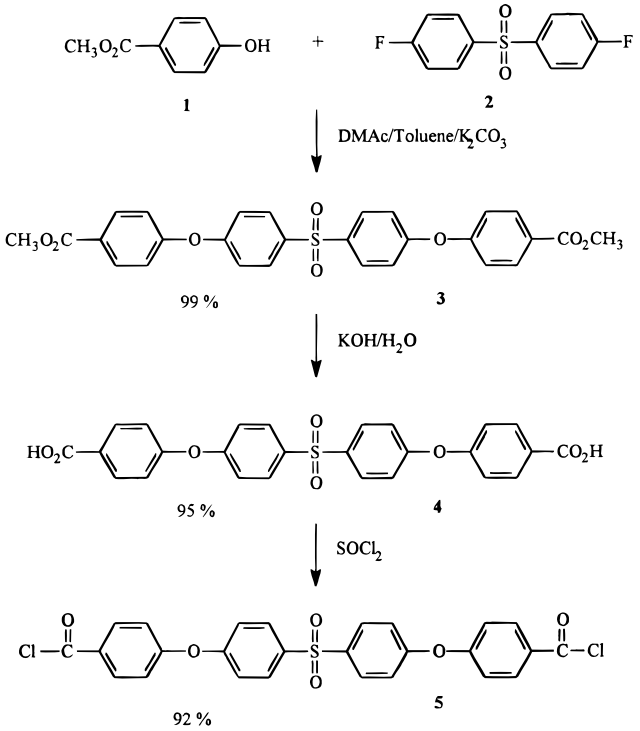
*Revised Manuscript Received February 26, 1997*

**Introduction.** The recent discovery by Brunelle and co-workers[1] of the high yield synthesis and facile polymerization of bisphenol-A based cyclic polycarbonates has sparked much interest in macrocyclic monomers. The advantages of macrocyclic precursors have been recognized in several respects, i.e., low melt viscosity and rapid melt ring opening polymerization without generating volatile side products. These features are particularly valuable for the manufacture of advanced composite materials. Other potential applications include reactive injection molding and structural adhesives. In the last several years, this area has been rapidly extended to other systems such as cyclic esters,[2] amides,[2,3] ether imides,[2] ether ketones,[4−6] and ether sulfones.[7−9] We have reported a number of polymerizable macrocycles synthesized by nucleophilic aromatic substitution reactions.[9−12]

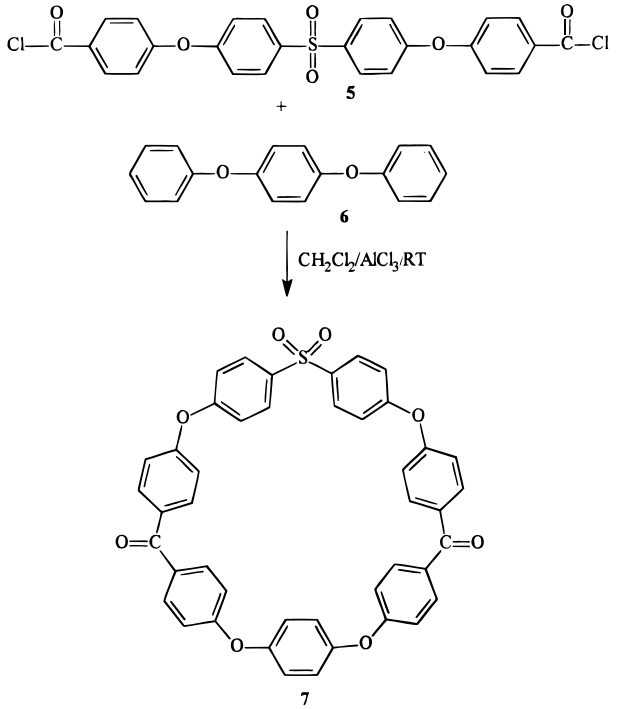
Although the Friedel−Crafts acylation reaction has been used to make linear poly(ether ketone)s, there has been no report of making use of this reaction to synthesize macrocyclic monomers. There are several potential advantages of using the Friedel−Crafts reaction for the synthesis of macrocycles. First, the reaction is generally very fast, which is very favorable for maintaining the pseudo high dilution condition and thus producing high yields. Second, the reaction temperature is relatively low, e.g., room temperature. In addition, the typical acylation solvents, such as methylene chloride, are inexpensive. Third, the starting materials, phenyl ethers and aromatic diacid chlorides, are inexpensive.

**Results and Discussion.** As with our previous approach,[9−12] we used a two-component cyclization method, which involves a short piece and long piece. The long piece was the diacid chloride **5**, which was prepared from methyl 4-hydroxybenzoate (**1**) and 4,4′-difluorodiphenyl sulfone (**2**) via ester **3** and acid **4** as outlined in Scheme 1.[13] Scheme 2 shows the Friedel−Crafts acylation cyclization of **5** with 4,4′-diphenoxybenzene (**6**). The pseudo high dilution condition was maintained by adding a solution of the two reactants from a dropping funnel to a large amount of solvent containing a suspension of anhydrous aluminum chloride. During the reaction, precipitation was observed. The precipitate was due to long linear oligomers. The macrocycle formed is fairly soluble in halohydrocarbon solvents, such as chloroform. The 35-membered macrocycle **7** was isolated by exhaustive extraction with hot acetone and

**Scheme 1**




**Scheme 2**

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S0024-9297(96)00373-7 CCC: $14.00 

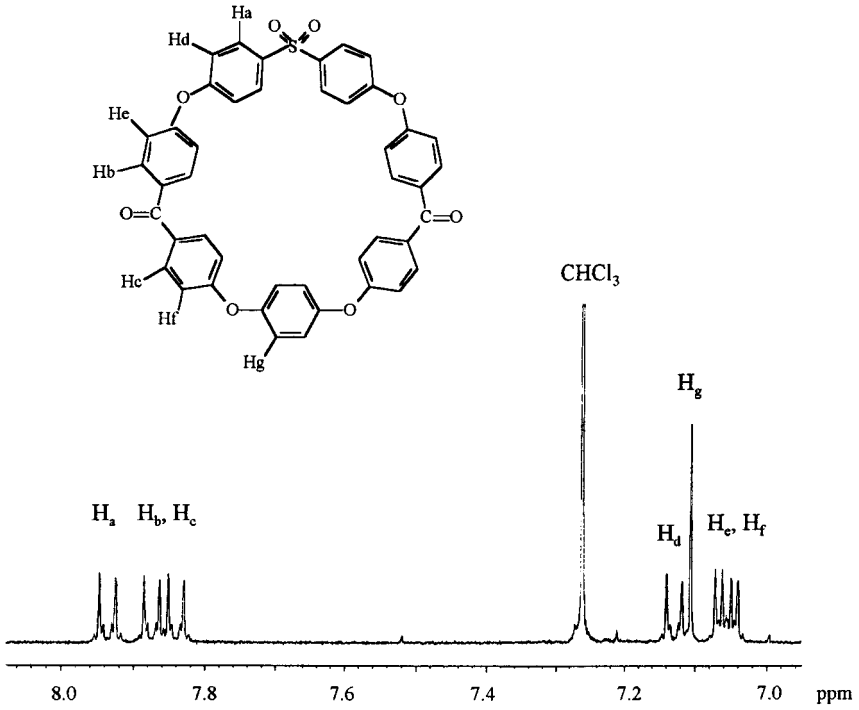


**Figure 1.** 400 MHz $^1$H NMR spectrum of macrocycle **7** in $CDCl_3$.

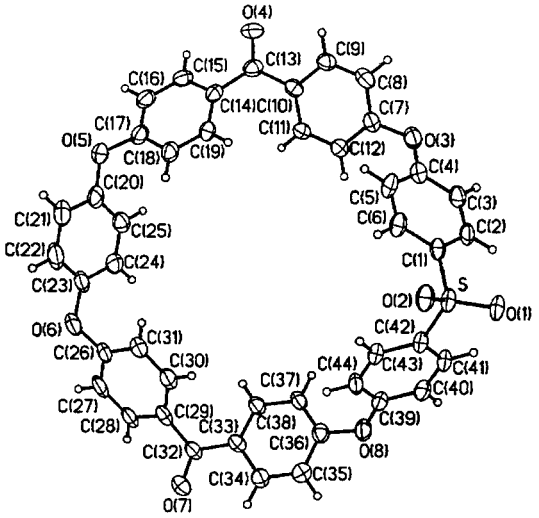


**Figure 2.** Single-crystal X-ray structure of macrocycle **7**.

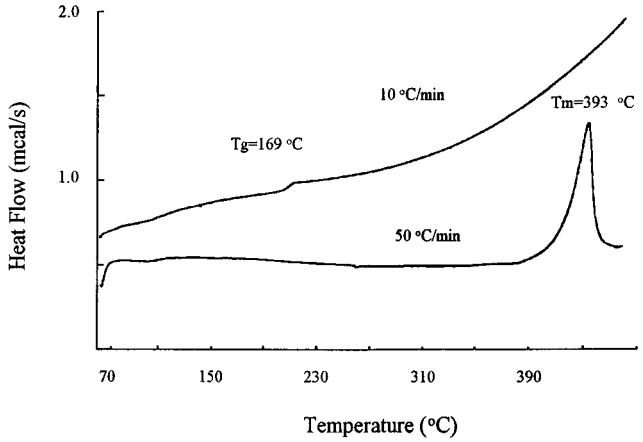


**Figure 3.** DSC thermograms of macrocycle **7** and a polymerized sample.

then purified using a silica gel column eluted with methylene chloride. The yield was 21%.

The unoptimized yield was quite low compared with that from the nucleophilic aromatic substitution method.[9−12] There are two major reasons for this fact. First, the reactants were added over about 3 h, which was fast compared with the approximately 30 h of addition time we typically used for nucleophilic substitution cyclizations.[9−12] Second, linear oligomers precipitated out during the reaction because the reaction concentration was too high. This is confirmed by the absence of the double sized, i.e., 70-membered macrocycle, in the crude product observed by MALDI-TOF mass analysis. Therefore, the major obstacle for high yield is the solubility. The problem may be solved by varying the solvent system and reaction conditions. It should be pointed out that according to our model study involving acylation of **6** and analogs with *p*-fluorobenzoyl chloride, the acylation took place exclusively at the para position.

The reverse phase HPLC chromatogram of **7** gave a single peak, indicating that the pure macrocycle was isolated.

Figure 1 gives the $^1$H NMR spectrum of macrocycle **7**. There are three doublets downfield, which correspond to the protons $H_a$, $H_b$, and $H_c$ ortho to the sulfone and carbonyl groups. The other three doublets located upfield are due to protons $H_d$, $H_e$, and $H_f$ ortho to the ether linkages. Due to the symmetry of the macrocycle, proton $H_g$ appears as a singlet at $\delta = 7.11$ ppm.

The size of the macrocycle was confirmed by the molecular ion peak at $m/z = 716$ in the mass spectrum. The structure of the macrocycle was conclusively proved by the single-crystal X-ray structure determination (Figure 2). The macrocycle adopts an open conformation, which is quite rigid.

The TGA thermogram of the macrocycle gives a 5% weight loss temperature of 500 °C at a heating rate of 10 °C/min in nitrogen. Figure 3 gives the DSC thermograms of the macrocycle and a polymerized sample. The macrocycle has a melting peak at 393 °C. The macrocycle was polymerized in the DSC with 4 mol%

CsF to give a polymer with a glass transition temperature at 169 °C, close to that predicted for a random copolymer of the three repeating units (EK, EEK, ES) on the basis of the Fox equation.

**Conclusions.** Although the yield was low compared with that of the aromatic nucleophilic substitution method,[5−12] we have demonstrated the potential use of the Friedel−Crafts acylation reaction to make macrocyclic monomers containing ether, ketone, and sulfone linkages. Future work will be directed toward optimization of the yield by choosing different solvent systems and extending this approach to other interesting cyclic systems. In fact we have by this methodology formed cyclic oligomers of ether ether ketone ether ketone (EEKEK) and ether ketone (EK).

**Acknowledgment.** The financial support of the Advanced Materials Synthesis and Processing Program (ARPA) via McDonnell-Douglas and the NSF Science and Technology Center for High Performance Polymeric Adhesives and Composites at Virginia Tech (DMR91-2004) is gratefully acknowledged.

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(13) Compounds **4** and **5** were reported by: Idage, S. B.; Idage, B. B.; Shinde, B. M. *J. Polym. Sci., Polym. Chem. Ed.* **1989**, *27*, 583. We found these compounds can be more conveniently prepared according to Scheme 1.

MA960373D