

**Macrocyclic Monomers:
Synthesis, Characterization and Ring-opening Polymerization**

by

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(ABSTRACT)

Interest in macrocyclic monomers can be dated back to the 1960's. The recent surge of research activities in this area is prompted by two facts: the encouraging discovery of high yield synthesis and facile ring-opening polymerization of cyclic polycarbonate; the need for a technique to solve the tough processibility problem of high performance polymers.

This work was intended to address the following aspects in the cyclic poly(ether ketone) or sulfone system.

The first goal was to understand the structure-property relationship of this type of macrocycles. A large number of macrocycles were synthesized by nucleophilic aromatic substitution cyclization reactions under pseudo-high dilution conditions. Pure individual macrocycles as well as cyclic mixtures were characterized by NMR, HPLC, GPC, FABMS, MALDI-TOF-MS, DSC and TGA. Comparison study suggests that the cyclic distribution is kinetically controlled. Several factors determine the melting points of individual macrocycles. The first factor is the ring size. A series of cyclic monomers for poly(ether ether ketone)s were synthesized and isolated. The melting point decreases as ring size increases. Single crystal X-ray structural results suggest that this phenomenon

is related to the increased flexibility of the larger sized macrocycles. The second factor is the functional groups of the macrocycles. X-ray structural and GPC experiments reveal that the sulfone group is more rigid than the ketone group, than ether group. The effect of functional groups on melting point is in the order sulfone>ketone>ether. A third factor is the symmetry of the macrocycles. Breaking the symmetry of macrocycle through comacrocyclization dramatically decreases the melting point of individual macrocycles as well as the cyclic mixture as a whole. Based on these findings, a novel two step method was developed to control the ring size distribution, which effectively reduced the amount of the small sized macrocycle and decreased the melting point.

In addition to the nucleophilic aromatic substitution cyclization, it was also demonstrated in this work that macrocycles can be synthesized by Friedel-Crafts acylation cyclization. However, this method is limited by the solubility problem.

The ring-opening polymerization of macrocyclic monomers was systematically studied. Several factors were considered in this study: the nature and amount of catalyst, temperature and time. CsF; metallic phenolate and Na₂S are good initiators. Conversion to near 100 % is possible under the controlled polymerization conditions. It was found that crosslinking is an inherent phenomenon. The molecular weight of the soluble fraction near complete conversion is almost independent of initiator and polymerization temperature. It is limited by the crosslinking reaction. It is demonstrated for the first time that the macrocyclic monomer techniques can be applied to more valuable

semicrystalline systems. Tough polymers such as high performance poly(ether ether ketone)s were produced through ring-opening polymerization.

The last chapter is devoted to the challenging synthesis of monodisperse poly(ether ether ketone)s. A convergent strategy was devised. A monofluoroaryl compound was synthesized by Friedel-Crafts acylation reaction. The final monodisperse linear oligomers were generated by reacting the monofunctional compound with a bisphenol through a quantitative reaction.

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APPENDEIX

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Chapter 1

Literature Review—Synthesis of Poly(ether ketone)s and sulfones and the Macrocyclic Monomer Technique

1.1 Introduction

Polymers are macromolecules built by linking together large numbers of smaller molecules. The pioneering work of Staudinger, Mark, Carothers and others in the 1920s and 1930s laid the foundation for the establishment of the structure-property relationships of polymeric materials. These pioneers paved the way for the innovative variety of synthetic polymers that has characterized the last half century.

The ease of manufacture and fabrication, wide range of physical and chemical properties and low raw-material costs have made polymers ubiquitous in our daily life, allowing us to replace in many cases, costly natural materials with cheap, attractive and often vastly superior polymeric materials. The widespread application of polymeric materials has generated the special need for high performance polymeric materials which can serve at high temperature, under high mechanical load and harsh environments. This has posed a strong challenge for polymeric materials scientists. Advances in polymerization and material processing techniques have enabled polymer scientists to develop a number of very successful high performance polymers such as KevlarTM, polymeric liquid crystalline polyesters, aromatic polyimides, poly(ether ketone)s and poly(sulfone)s, to name a few. The polymeric materials with toughness,

high strength, high modulus, as well as high temperature and solvent resistance must be structurally rigid on the molecular scale. This results in inherently poor solubility, high softening point and high viscosity and thus poor processibility of these materials. Reactive processing is a technique targeted at the processibility of these high performance polymer materials. In this technique, low molecular weight polymers with reactive functional groups or cyclic structures are chain extended, crosslinked or ring-opening polymerized when the viscosity is low and during that time the polymer is formed and processed.

Poly(ether ketone)s (PEK) and poly(ether sulfone)s (PES) are classes of high performance materials that may display excellent mechanical properties, high thermal and environmental stability, solvent and hydrolytic resistance. There has been a lot of interest in these types of materials. The focus of this work is the synthesis and ring-opening polymerization of macrocyclic monomers to generate high performance PEK and PES with the ultimate goal of solving processibility problems associated with these types of materials. Making PEK and PES through macrocyclic precursors offers several advantages, e. g., low melt viscosity and rapid polymerization without generating side product. In this chapter, the syntheses of PEK and PES as well as the macrocyclic monomer technique will be reviewed.

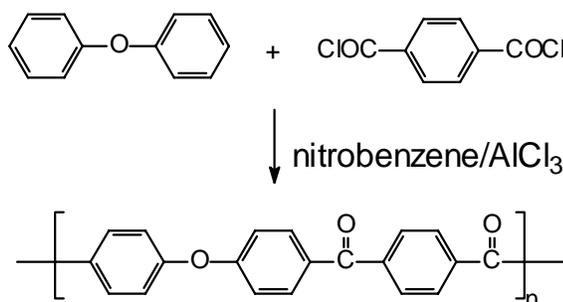
1.2 Synthesis of Poly(ether ketone)s and Poly(ether sulfone)s

A. Electrophilic Route

Traditionally, PEK and PES have been synthesized by two types of reactions: Friedel-Crafts acylation or sulfonation polycondensation and nucleophilic aromatic substitution (S_NAr) polycondensation.

PEK are generally semicrystalline polymers with limited solubility in common organic solvents. The early research in this area was focused on finding a suitable solvent system for the synthesis of PEK by Friedel-Crafts acylation polycondensation.

Scheme 1.1



Bonner¹ at DuPont pioneered the synthesis of PEK through Friedel-Crafts acylation. He used terephthaloyl chloride and diphenyl ether in nitrobenzene solution with a catalyst such as aluminum chloride or antimony pentachloride (Scheme 1.1). However, only low molecular weight polymers were obtained. At the same time, ICI researchers used similar chemistry but different reaction conditions. Goodman² used methylene chloride as the solvent. Polymers with

[1] Bonner, W. H., US Patent 3,065,205 (1962).

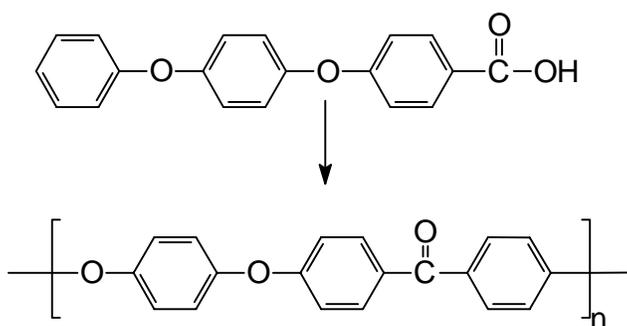
[2] Goodman, I.; McIntyre J. E.; Russell, W. British Patent 971, 227 (1964).

moderate molecular weights were obtained. Under the same conditions, condensation of an AB monomer p-phenoxybenzoyl chloride afforded a high molecular weight poly(ether ketone).

Iwakura and coworkers found that polyphosphoric acid can be used as an alternative solvent to condense p-phenoxybenzoic acid to form PEK with moderate success.³

A breakthrough in the synthesis of PEK was made by Marks when the HF/BF₃ solvent system was found.⁴ The polyacylation reaction in HF/BF₃ proceeds very rapidly. The reactant concentration should be kept between 0.5 - 1.0 M. Low concentration favors the formation of cyclics and high temperature causes side reaction such as formation of triarylcarbonium ions. Reaction temperature should be below 30 °C to avoid undesirable side reactions. Under well controlled reaction conditions, it is possible to get high molecular PEK with more than 100 repeating units.

Scheme 1.2



[3] Iwakura Y.; Uno, K. Takiguchi, T. *J. Polymer Sci.*, Part A-1 **1968**, 6, 3345.

[4] Marks, B. M. US Patent 3, 441, 538 (**1964**).

Rose and coworkers at ICI discovered that trifluoromethanesulfonic acid can be used as the solvent as well as the catalyst for polyacylation.⁵ This method has been successfully applied to polymerize 4-(4'-phenoxy)phenoxybenzoic acid to prepare a polymer with an inherent viscosity of 1.19 (Scheme 1.2).

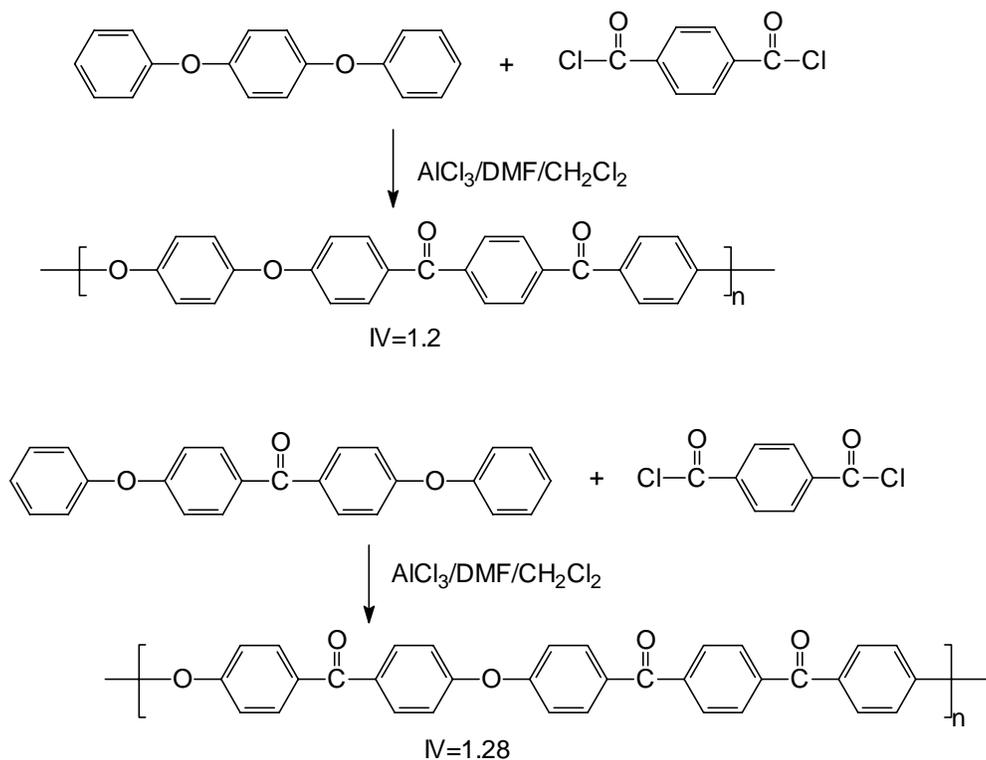
However, HF/BF₃ is not easy to handle and the polymerization has to be carried out on a vacuum line. Trifluoromethanesulfonic acid is very expensive and neither solvent is attractive for industrial applications. There has been renewed interest in using the methylene chloride/aluminum chloride system, but the solubility problem has to be solved. Jansons and coworkers⁶⁻⁷ at Raychem found that Lewis bases such as DMF, tetramethylene sulfone, dimethyl sulfone, butyronitrile, lithium chloride and sodium chloride could act as swelling media or as solvents for the polymer to give high molecular weight polymers. The researchers found that the Lewis bases can complex with the aluminum chloride. The complexes are best prepared in chlorinated hydrocarbon solvents at temperatures below 0 °C. The polymers synthesized by this method are para-linear and free from defect structures. A number of high molecular weight polymers were generated using their technique (Scheme 1.3)

[5] Rose J. B. European Patent 63, 874 (1982).

[6] Jansons, V.; Gors, H. C. WO 84 03, 892 (1984).

[7] Jansons, V.; Dahl, K. *Macromol. Chem., Macromol. Symp.* **1991**, 51, 87.

Scheme 1.3

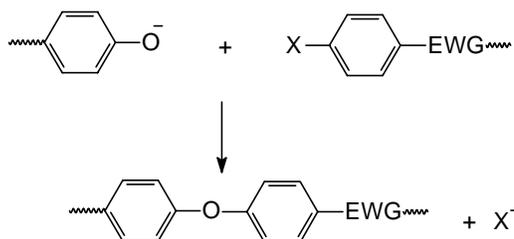


Analogously, PES can be synthesized by Friedel-Crafts sulfonylation. In contrast to the acylation reaction, the preferred catalyst is ferric chloride instead of aluminum chloride. The amount of catalyst is normally 0.1-4 wt%. The sulfonylation can be carried out in the melt state at temperatures below 250 °C. However, normally there is a significant amount of insoluble product generated due to sulfonylation at the ortho position.

B. Nucleophilic Route

In contrast to the electrophilic route, the nucleophilic aromatic substitution reaction involving bisphenoxide and activated dihalide is more controllable and high molecular weight polymers can be more easily obtained from bisphenols and activated dihalides. This reaction can be generalized as in Scheme 1.4.

Scheme 1.4



X is the leaving group such as F, Cl, NO₂; EWG= CO, SO₂, SO, phosphine oxide, etc.

Electron withdrawing groups such as sulfone, carbonyl, sulfoxide or phosphine oxide are necessary to activate the aromatic dihalides. The reactivities of aromatic halides are in the order of F>>Cl>Br. In general, with a strong electron withdrawing group such as sulfone, the leaving group can be F⁻ or Cl⁻. In the case of weak withdrawing groups, the leaving group should be F⁻ to get high molecular weight polymer. For the less reactive monomers, such as 4, 4'-dichlorobenzophenone, single electron transfer side reactions were observed;⁸⁻⁹ these prevent building up high molecular weight. Percec's group¹⁰ tried polymerization with dichloroketone monomers, but the ability to achieve high molecular weight poly(ether ketone)s was not consistently demonstrated.

[8] Percec, V.; Clough, R. S.; Grigoras, M.; Rinaldi, P. L.; Litman, V. E.,

Macromolecules **1993**, 26, 3650.

[9] Percec, V, Clough R. S., Rinaldi, P. L., Litman, V. E. *Macromolecules* **1991**, 24, 5889.

[10] Percec, V.; Grigoras, M.; Clough, R. S. Fanjul, J. *J. Polym. Sci: Part A: Poly. Chem.* **1995**, 33, 331.

DMSO was used as the solvent in the pioneering work of Johnson and coworkers.¹¹ Sodium hydroxide was the base to deprotonate the bisphenol to generate the reactive bisphenoxide. Chlorobenzene was the azeotropic solvent to remove the water from the system. Strict stoichiometry of the bisphenol and sodium hydroxide is required as excess sodium hydroxide can attack the activated dihalide or the ether linkage of the polymer, which will reduce the molecular weight. Another drawback of using sodium hydroxide as the base is the insolubility of the sodium phenoxide, which prevents successful polymerization.

McGrath's group¹² found that alkali metal carbonates such as sodium and potassium carbonate can be substituted for sodium or potassium hydroxide as the base. Excess carbonate can be tolerated because the carbonate is a poor nucleophile.

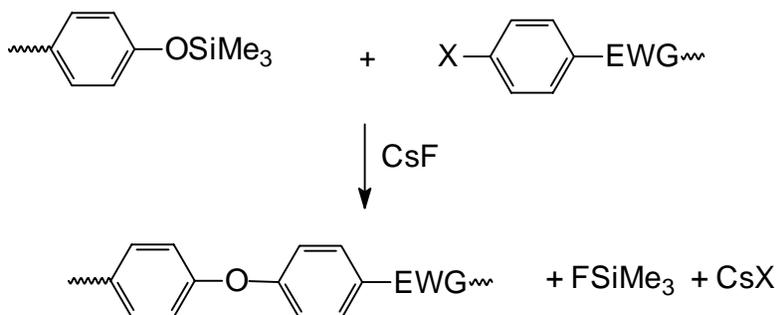
The preferred solvents for the S_NAr polycondensation polymerization are dipolar aprotic solvents such as DMAc, DMSO and NMP. However, para linked PEK will precipitate from the solution and as a result only low molecular weight polymer can be obtained. Rose and coworkers¹³ found that diphenyl sulfone is an inert high temperature solvent which permits polymerization near the melting

[11] Johnson, R. N.; Farnham, A. G.; Clendinning, R. A.; Hale, W. F. Merriam, C. N. *J. Polym. Sci., Part A-1* **1967**, 5, 2375.

[12] Mohanty, D. K.; Sachdeva, Y.; Hedrick, J. L.; Wolfe, J. F.; McGrath, J. E. *Am. Chem. Soc. Div. Polym. Chem. Polym. Prepr.* **1984**, 25, 19.

points of the polymers. The discovery effectively solved the solubility problem and eventually led to the commercialization of poly(ether ether ketone) (PEEK).

Scheme 1.5



Kricheldorf and Bier¹⁴⁻¹⁵ invented a synthesis of poly(arylene ether)s from silylated bisphenols as shown in Scheme 1.5. The activated cesium phenoxide is generated with CsF as the catalyst. A unique feature of Kricheldorf's synthesis is that the polymer is produced in the melt. The side product trimethylsilyl fluoride is a volatile compound, which is removed at high temperature. Polymer is obtained in pure form without the need to remove the solvent and the salts. For example, high molecular weight PEEK was produced by this method.

Müllen and coworkers¹⁶⁻¹⁷ found that the reactivity of a bisphenoxide can be increased by adding some high temperature phase transfer catalyst such as

[13] Rose, J. B.; Staniland, P. A. US Patent 4,320,224 (1982).

[14] Bier, G. ; Kricheldorf, H. R. US Patent, 4, 474,932 (1984).

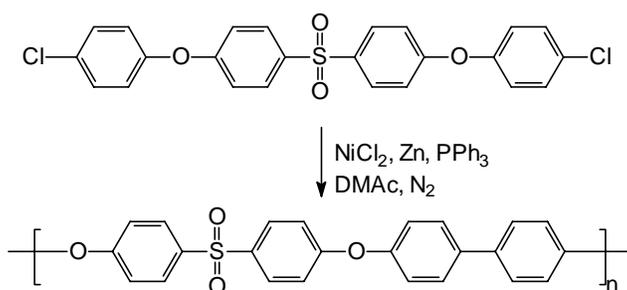
[15] Kricheldorf, H. R.; Bier, G. *Polymer* **1984**, 25, 1151.

[16] Hoffman, U.; Klapper, M.; Mullen, K. *Polym. Bull.* **1993**, 30, 481.

N-alkyl-4-(dialkylamino)pyridinium chlorides in the polymerization medium. Thus relatively inexpensive dichloride monomers can be used instead of the difluorides. They were able to prepare high molecular PEEKK with an inherent viscosity of 0.9 dL/g compared with a value of less than 0.3 dL/g without the catalyst.

C. Carbon-Carbon Coupling Route

Scheme 1.6



The ether sulfone group can be pre-made in the monomers and the poly(ether sulfone)s then synthesized by C-C coupling reactions. This technique has been successfully applied to synthesize a number of polysulfones.¹⁸ An example is shown in Scheme 1.6. There are several key factors for the

[17] Hoffmann, U.; Helmer-Metzmann, F.; Klapper, M.; Mullen, K.

Macromolecules **1994**, *27*, 3575.

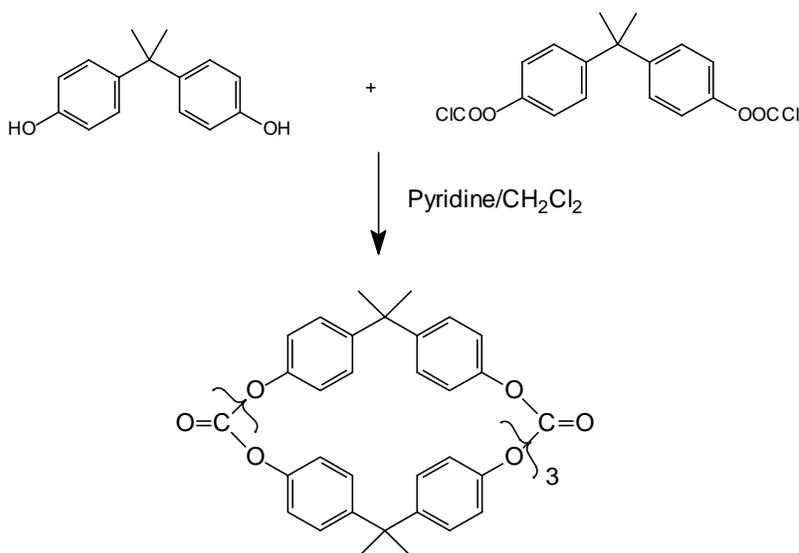
[18] Kwiatkowski, G. T.; Colon, I. in "Contemporary Topics in Polymer Science", vol. 7, Salamone, J. C. and Riffle, J. S. Ed., Plenum Press, New York, **1992**, pp. 57.

polymerization to be successful. The system should be free from water and oxygen, and the zinc should be of high quality.

1.3 Macrocyclic Monomers-Synthesis and Polymerization

A. Cyclic Polycarbonates and Polyesters

Scheme 1.7

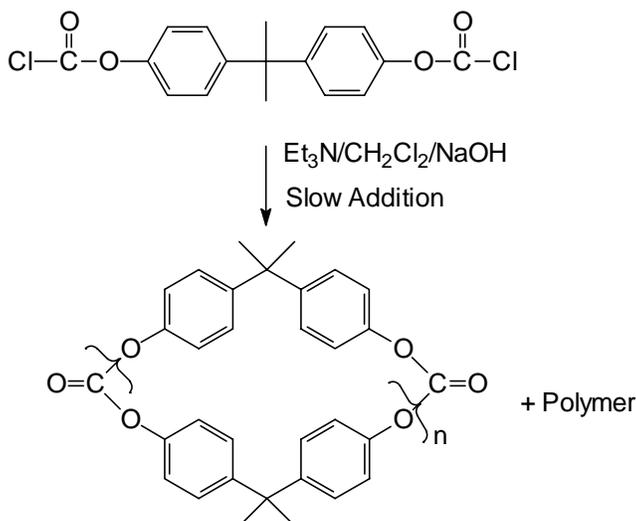


Interest in cyclic polycarbonate can be dated back to the 1960's. In 1962, Schnell and Bottenbruch¹⁹ reported the preparation of the cyclic tetrameric carbonate of bisphenol-A. Their synthesis was carried out in methylene chloride by reacting bisphenol-A with its bischloroformate in the presence of excess pyridine under a high dilution condition of 0.05 M (Scheme 1.7). The yield was only 21 %. Other similar macrocycles were also synthesized using different bisphenols. Polymerization of the macrocycle at the melting point was observed.

[19] Schell, H.; Bottenbruch, L. *Macromolecular Chem.* **1962**, 57, 1.

In 1965, Prochaska²⁰ reported preparation of the cyclic trimeric carbonate of bisphenol-A using similar high dilution techniques.

Scheme 1.8



There had been little activity with the cyclic polycarbonate system until Brunelle and coworkers at General Electric Company made a breakthrough.²¹⁻²³ They found that under pseudo-high dilution conditions cyclic polycarbonate was formed selectively. In a typical experiment, the pseudo-high dilution condition is maintained by adding bisphenol-A bischloroformate slowly to an efficiently stirred mixture of triethylamine, aqueous sodium hydroxide and methylene

[20] Prochaska, R. J. US patent 3,221,025 (1965).

[21] Brunelle, D. J.; Boden, E. P.; Shannon, T. G. *Am. Chem. Soc. Div. Polym. Chem. Polym. Prepr.* **1989**, 30(2), 569.

[22] Brunelle, D. J.; Boden, E. P.; Shannon, T. G. *J. Am. Chem. Soc.* **1990**, 112, 2399.

[23] Brunelle, D. J.; Shannon, T. G. *Macromolecules* **1991**, 24, 3035.

chloride (Scheme 1.8) . The selectivity for cyclics vs linear is about 10000 to 1. Two major processes are involved in the reaction scheme, i. e., the hydrolysis of chloroformate to form phenoxide and condensation of the chloroformate with the phenoxide to form carbonate. The cyclization reaction is controlled by the ratio of hydrolysis to condensation. In the case of excessive hydrolysis, formation of linear oligomers or complete hydrolysis of BPA will occur. Conversely, if hydrolysis occurs too slowly, the concentration of BPA-bischloroformate will increase, eventually leading to conditions favoring intermolecular reactions, forming the linear polymer. The key to their success is the finding of suitable reaction conditions to maintain the correct hydrolysis/condensation ratio, while keeping the reactions fast enough to prevent buildup of reactive intermediates. Thus the concentration of the reactants remains very low to favor the intramolecular cyclization reaction. The catalyst is the most crucial factor accounting for the high selectivity of cyclics vs linear oligomers.²⁴⁻²⁵ Substituting triethylamine with pyridine under otherwise identical reaction conditions leads to selective formation of linear oligomers, while the formation of cyclics is totally excluded. The results vary widely using other amines, bases, or phase transfer catalysts ranging from linear oligomers, cyclic oligomers, high-molecular weight polymer, to no reaction. The amine used as the cyclization catalyst must be

[24] Boden, E. P. Brunelle, D. J. Shannon, T. G. *Am. Chem. Soc. Div. Polym. Chem. Polym. Prepr.* **1989**, 30(2), 571.

[25] Boden, E. P.; Brunelle, D. J. in "Topics in Polymer Science", vol.7. Salamone J. C. and Riffle, J. S. ed., Plenum Press, NY, **1992**. pp. 21.

nucleophilic and soluble in the organic phase. Mechanistic studies suggested that the effectiveness of an amine catalyst is related to its ability to react with the chloroformate to form an acylammonium salt. The amine catalyst is also necessary for the hydrolysis of the chloroformate.

The cyclics can be isolated by the solubility difference between the high molecular weight polymer and the cyclics in acetone. The typical product was composed of cyclic oligomer and high-molecular weight polymer in a ratio of about 85/15. The number of repeating units in the cyclics ranges from 2 to 26, with 2-10 composing 90 % of the total. Gel permeation chromatography indicated that the mixture had an average molecular weight of 1300, corresponding to a pentamer. The mixed cyclic oligomers have a melting point between 200-210 °C. Due to their low molecular weight, the cyclic oligomer carbonates have melt viscosities about four orders of magnitude lower than the commercial linear polymers.

A number of transesterification initiators can be used to initiate the ring-opening polymerization of the cyclic polycarbonate mixture.²⁶⁻²⁷ These initiators include tetra(4-trifluoromethylphenyl)borate tetrabutylammonium salt, sodium fluoride, sodium chloride, sodium bromide, lithium phenoxides and lithium carboxylates. They are nucleophilic in nature and can induce anionic ring-

[26] Evans, T. L.; Berman, C. B.; Carpenter, J. C.; Choi, D. Y. Williams, D. A. *Am. Chem. Soc. Div. Polym. Chem. Polym. Prepr.* **1989**, 30(2), 573.

[27] Stewart, K. R. *Am. Chem. Soc. Div. Polym. Chem. Polym. Prepr.* **1989**, 30(2), 575.

opening polymerization. Very high molecular weight polymers can be obtained when small amounts of initiators are used (<1 mol %). The polymerization is athermal because only the cyclic dimer has some ring-strain and its amount is very small (1-5 %). The polymerization is not truly living because the ring-opening and chain exchange have approximately the same rates. But the polymerization does show some characteristics of living polymerization. For example, after the cyclics are consumed, addition of more monomer will increase the molecular weight and if more initiator is used molecular weight will be decreased. Control of the molecular weight can be achieved by adding bisphenols or diphenyl carbonate as chain transfer agents.

In order to apply the ring-opening polymerization technique to various situations, it is necessary to have controlled polymerization, i. e., polymerization after the low viscosity oligomers have wetted composite fibers. Researchers at GE recently developed a two component initiator system.²⁸ Neither component will initiate the ring-opening polymerization separately. However, when the two components are mixed together, a nucleophile is generated to start the polymerization. Their two component system is based upon triphenylphosphine and alkyl halide. The two react with each other to form the quaternary phosphonium halide, which is an effective initiator. However, the problem with their approach is the incomplete conversion (81-86 %) of the cyclics to linear polymers.

[28] Krabbenhoft, H. O.; Brunelle, D. J. ; Pearce, E. J. A. *Am. Chem. Soc. Div. Polym. Chem. Polym. Prepr.* **1995**, 36(2),209.

The resulting polycarbonate has properties essentially equivalent to commercial polycarbonate²⁹. The molecular weight is limited by the exchange reaction. The molecular weight normally obtained is about 300,000. At the end of polymerization, the polymer shows a polydispersity of about 2.0.

Brunelle and coworkers extended their work by substituting some bisphenol-A with other bisphenols to make a number of new macrocycles, which contain functional groups such as amide, ketone, sulfone and amide etc.³⁰ (Table 1.1). These cyclics were successfully ring-opening polymerized to afford high molecular weight polymers. Substituting bisphenol-A with some hydroquinone³¹⁻³² resulted in improved solvent resistance of the final polymer without sacrificing mechanical properties.

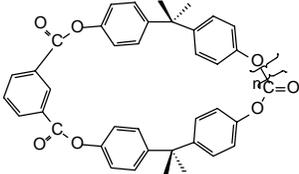
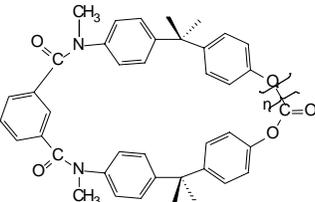
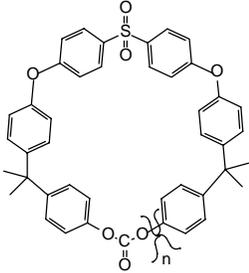
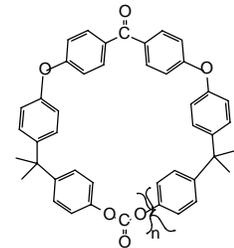
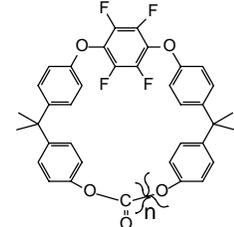
[29] Evans, T. L.; Berman, C. B.; Carpenter, J. C.; Choi, D. Y. Williams, D. A. *Am. Chem. Soc. Div. Polym. Chem. Polym. Prepr.* **1989**, 30(2), 573.

[30] Brunelle, D. J. in "Topics in Polymer Science", vol.7. Salamone J. C. and Riffle, J. S. ed., Plenum Press, NY, **1992**. pp. 21.

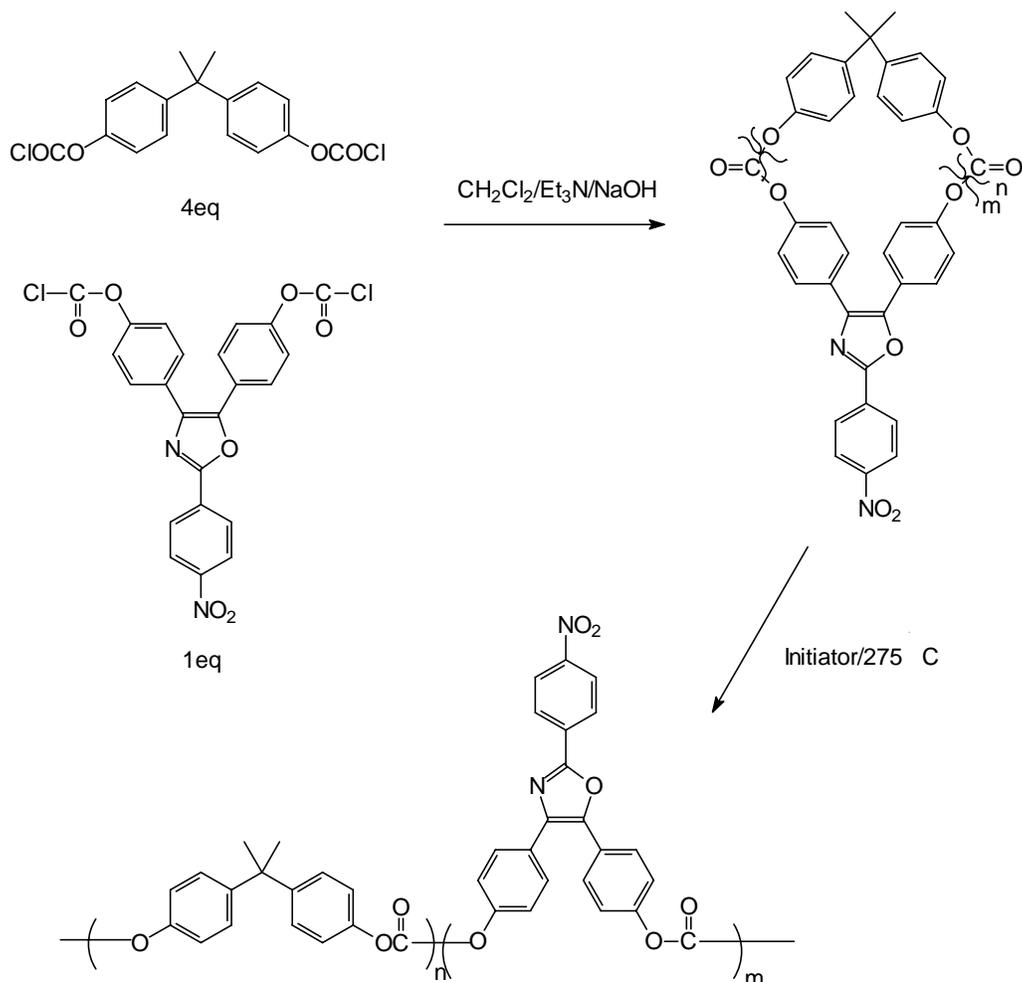
[31] Brunelle, D. J. Krabbenhoft, H. O. Bonauto, D. K. *Am. Chem. Soc. Div. Polym. Chem. Polym. Prepr.* **1992**, 33(1), 73.

[32] Brunelle, D. J. *TRIP* **1995**, 3(5).

Table 1.1 Cyclic carbonates containing various functional groups and molecular weight and T_g of polymers obtained from ring-opening polymerization

Cyclic	Yield	$10^{-3}M_w$	T_g ($^{\circ}C$)
	80	67	167
	95	48	154
	90	48	169
	92	88	165
	88	48	128

Scheme 1.9

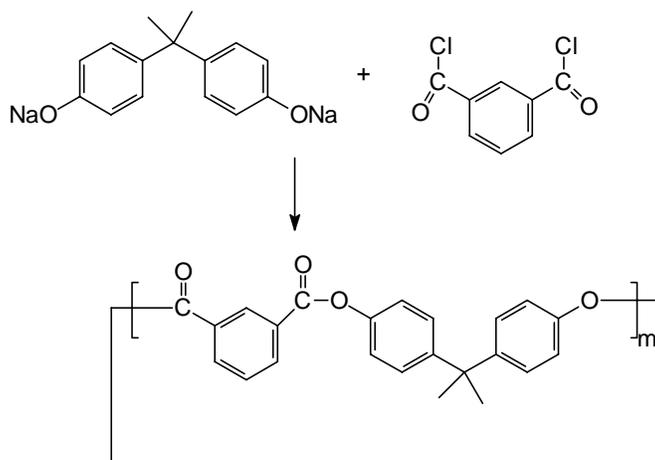


Brittain's group³³ made a very interesting extension of Brunelle's synthesis of cyclic polycarbonate. They came up with the idea of introducing non-linear optical (NLO) groups into the structure. They hoped that by ring-opening the cyclics under electric poling an NLO polycarbonate would be obtained with non-centrosymmetric alignment of the dipoles. They first synthesized the bischloroformate containing an NLO chromophore, which was then cocyclized

[33] Kulig, J. J.; Brittain, W. J.; Gilmour, S.; Perry, J. W.; *Macromolecules* **1994**, *27*, 4838.

with four equivalents of bisphenol-A chloroformate (Scheme 1.9). ^1H NMR indicated 13 % of the chromophore was included in the cyclics. The cyclic mixture was successfully ring-opening polymerized with titanium diisopropoxide bis(2,4-stanedionite) at 275 °C to give a polymer with a M_n of 6.4kg/mol. But no study of the nonlinear optical properties of the final polymer was reported.

Scheme 1.10

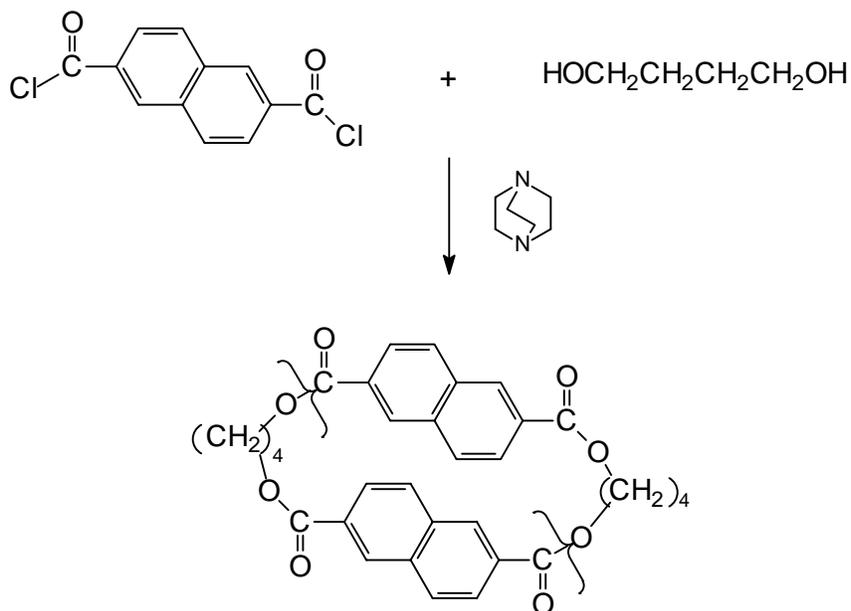


The success of the cyclic polycarbonate system prompted researchers at GE to extend their work to aromatic macrocyclic polyester systems. These cyclic polyesters were similarly produced by an interfacial cyclization reaction (Scheme 1.10). Guggenheim and coworkers³⁴ reported synthesis of cyclic aromatic polyesters based on bisphenol-A and iso- or tere-phthaloyl dichloride. The best yield was around 65 %. However, when the spirobiindane bisphenol

[34] Guggenheim, T. L.; McCormick, S. J.; Kelly, J. J.; Brunelle, D J.; Colley, A. M.; Boden, E. P.; Shannon, T. G. *Am. Chem. Soc. Div. Polym. Chem. Polym. Prepr.*, **1989**, 33(2), 138.

was used, cyclic yield was as high as 85 %. Polymerization of these cyclics was demonstrated and high molecular weight polymers were obtained.

Scheme 1.11



Brittain's group³⁵ reported synthesis of cyclic poly(butylene naphthalene) oligomers from 2,6-naphthalene dicarbonyl chloride and 1,4-butanediol using diazabicyclo[2,3,2]octane catalyst as shown in Scheme 1.11. The cyclics were obtained by extraction with methylene chloride to get a crude yield of 75 %. The cyclics were ring-opening polymerized with dibutyl tin oxide at 275 °C for 15 minutes to give the corresponding linear polymer. However, a polymer with a low inherent viscosity of 0.28 dL/g was obtained.

[35] Hubbard, P.; Brittain, W. J. Simonsick, W. J. Ross, C. W. *Macromolecules*,

1996, 29, 8304.

Hodge's group³⁶ has developed a very novel approach to the synthesis of cyclic polyester oligomers. The monomers they used were ω -halogenocarboxylic acids. These monomers were attached to a commercial strong-base anion exchange resin as the carboxylate salts. On heating a suspension of the bonded carboxylate salts polymerization occurred by displacing halide with carboxylate anion. The linear chain that was formed remained attached to the insoluble resin via the carboxylate end group. However, the cyclic formed by the same reaction was not bonded to the insoluble support. Thus the linear oligomers and the cyclics can easily be separated.

B. Cyclic Poly(ether ketone)s and Cyclic Poly(ether sulfone)s

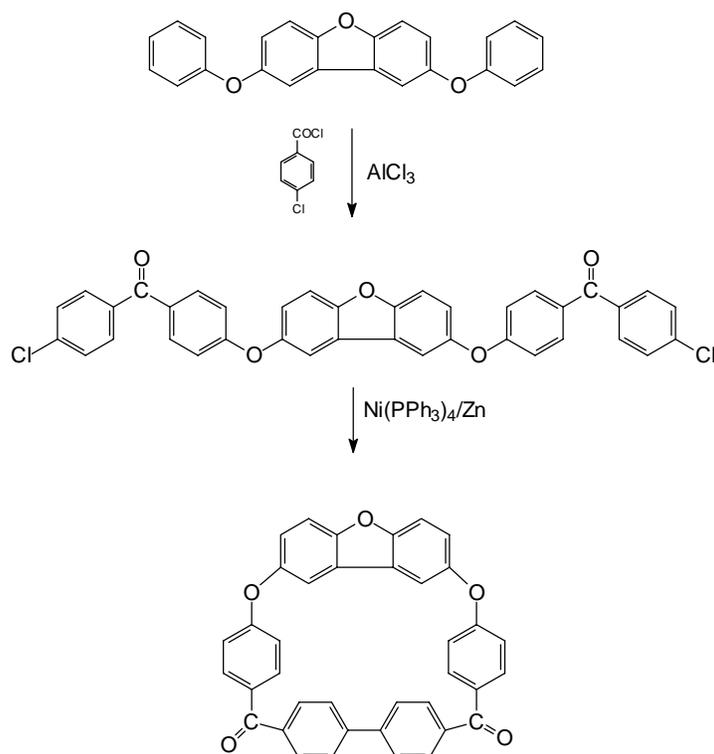
Following Brunelle's creative work on high yield synthesis and facile ring-opening polymerization of cyclic polycarbonate, there has been proliferation of work on other types of macrocyclic monomers. Colquhoun's group³⁷ at ICI was the first to report the synthesis of macrocyclic monomers containing ether ketone or ether sulfone linkages. The ether ketone or ether sulfone functional groups were pre-made in the precursors. The cyclization was achieved by recently developed nickel-promoted coupling of aryl halides (Scheme 1.12). Pseudo-high dilution conditions were maintained by progressive addition of

[36] Hodge, P.; Houghton, M. P.; Lee, M. S. K. *J. Chem. Soc., Chem. Commun.* **1993**, 581.

[37] Colquhoun, H. M.; Dudman, C. C.; Thomas, M.; O'Mahoney, C. A.; Williams, D. J. *J. Chem. Soc., Chem. Commun.* **1990**, 336.

starting materials in DMAc to a solution containing an equimolar amount of $\text{Ni}(\text{PPh}_3)_4$ generated in situ. The cyclic yield was about 40 %. The isolation of cyclics was made possible by the solubility difference between the cyclics and the linear by-products.

Scheme 1.12

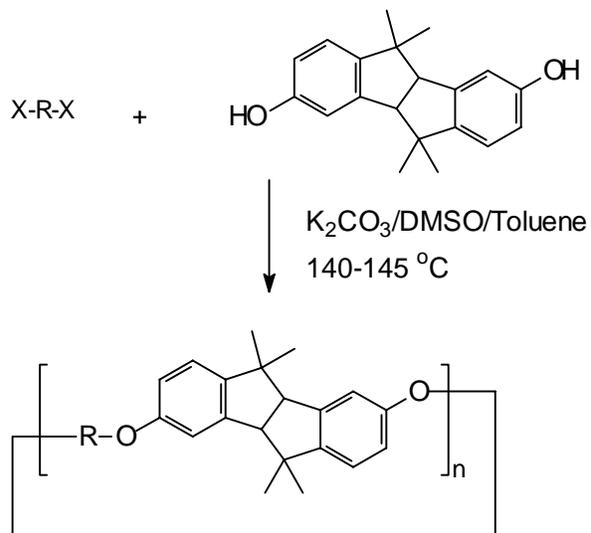


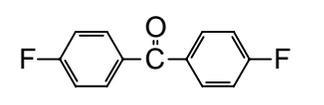
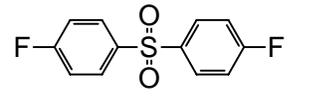
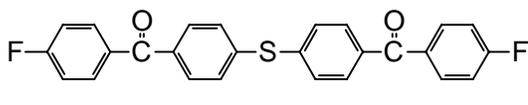
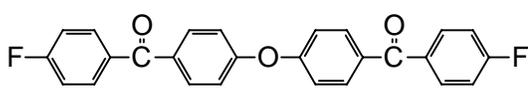
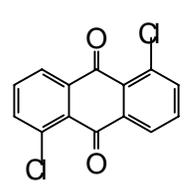
They were also the first group to realize that ring-opening polymerization of this type of ether ketone or ether sulfone macrocycles is possible by the ether exchange mechanism with nucleophilic initiators such as cesium fluoride or metallic phenolates. They successfully polymerized the macrocycle in the presence of catalytic amounts (1-5 mol %) of nucleophilic initiators such as cesium fluoride or the potassium salt of 4-hydroxybenzophenone. The polymerization, which is strongly exothermic due to the highly strained structure

of the macrocycle, was complete within 2-5 minutes, depending on the reaction temperature and the amount of initiator. After polymerization, the resulting amorphous polymer was tough and transparent. However, it was only slightly soluble in concentrated sulfuric acid, indicating some crosslinking reaction had taken place. This polymer has a glass transition temperature of 225 °C. If a small amount of endcapping agent such as 4-benzoyl-4'-(p-fluorobenzoyl)biphenyl was added, a completely soluble polymer with inherent viscosities of 0.40-0.70 dL/g was achieved.

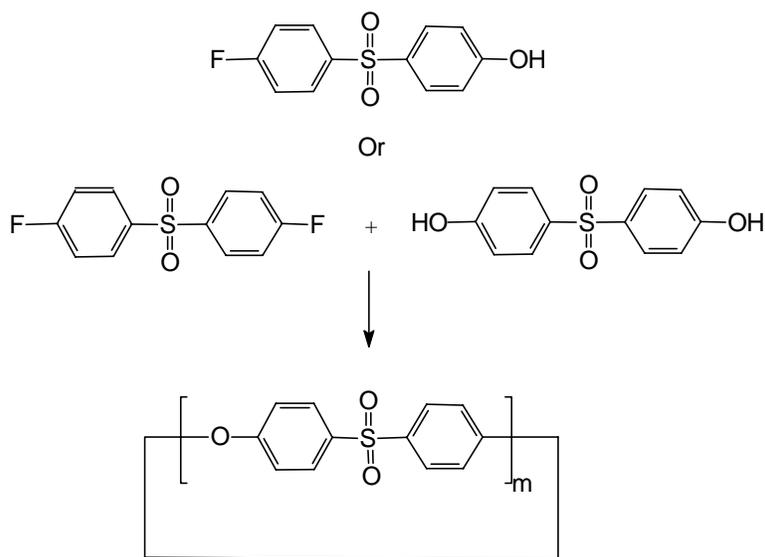
At almost the same time, researchers at General Electric Company also reported their synthesis of cyclic poly(ether ketone)s and poly(ether sulfone)s by a different method, i. e., nucleophilic aromatic substitution reaction (Scheme 1.13). They used the typical carbonate process in DMSO without using the pseudo-high dilution condition and the reactant concentration was as high as 67 mM. Good yields were obtained. The key to their synthesis was the use of spirobiindane containing monomers. The structural rigidity and orthogonal orientation of the configuration of the spirobiindane group favors cyclization. Ring-opening polymerization of the cyclic ether sulfone was only sketchily described. The cyclic oligomeric mixture was polymerized with 10 mol % of the disodium salt of bisphenol-A at 380-400 °C for 15 minutes to give a polymer with weight average molecular weight of about 80 kg/mol. But ring-opening polymerization of other macrocycles was not reported.

Scheme 1.13



X-R-X	Cyclic Yields (%)
	47
	45
	48
	40
	52

Scheme 1.14



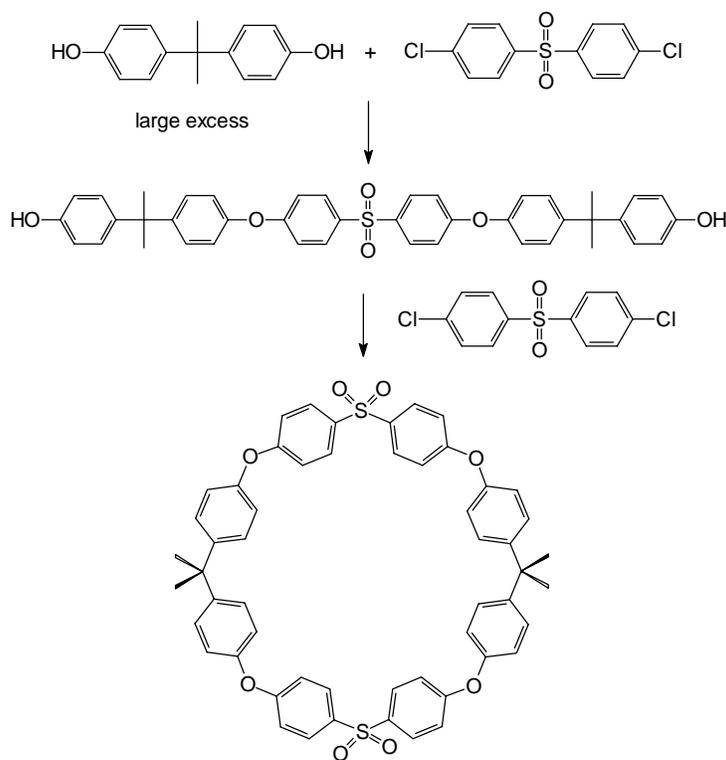
In 1991, Mullins and coworkers at Dow Chemical Company reported synthesis of cyclic poly(ether sulfone)³⁸ (Scheme 1.14). In their typical reaction conditions, solutions of 4,4'-difluorodiphenylsulfone and aqueous KOH were added simultaneously to a refluxing solution of DMSO. The bisphenol was generated *in situ* to give a cyclic yield of 55 %. The isolated cyclic trimer and tetramer are high melting point compounds. However, the mixture of cyclics is amorphous and begins to flow at around 250 °C. Mullins et al. pointed out that the key condition is to maintain the concentrations of reactants as low as possible. Correct stoichiometry is another important factor. The cyclic poly(ether sulfone) mixture was polymerized with CsF at 300 °C for 2 hours to give a polymer having an inherent viscosity of 0.5 dL/g, which is comparable to

[38] Mullins, M. J.; Woo, E. P.; Chen, C. C.; Murray, D. J. ; Bishop, M. T. Bacon, K. E. *Am. Chem. Soc. Div. Polym. Chem. Polym. Prepr.* **1991**, 32(2), 174.

commercially available poly(ether sulfone). They also synthesized a number of other cyclic polyether mixtures to demonstrate the generality of the method.

One problem these researchers had was the spontaneous ring-opening polymerization of the cyclic mixtures without added initiator.³⁹ They attributed this problem to residual salt. It was found that passing a solution of the cyclic oligomers in DMAc through a strong acid ion exchange column gave melt stability. The viscosity of the cyclic melt is orders of magnitude lower than that of corresponding linear polymers.

Scheme 1.15



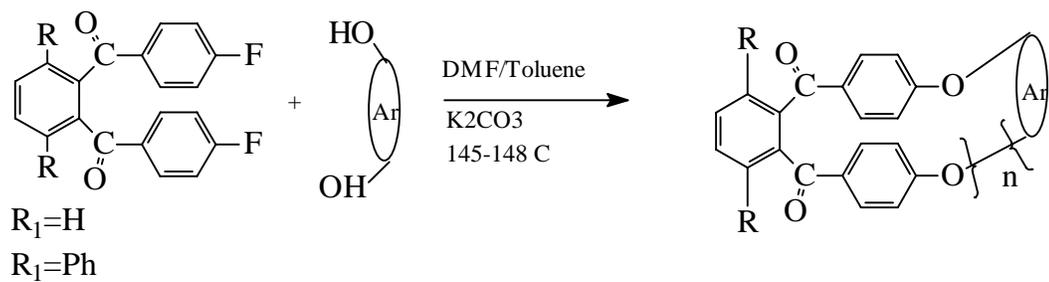
[39] Mullins, M. J.; Woo, E. P.; Murray, D. J.; Bishop, M. T. *Chemtech* **1993**, (August), pp. 25-28.

In 1993, Gibson and Ganguly⁴⁰ reported their synthesis of a diether disulfone macrocycle. Their interest was to use the aromatic cyclics as cyclic components for the synthesis of polyrotaxanes. In their synthesis, a two step approach was used (Scheme 1.15). In the first step an extended bisphenol was synthesized by using a large excess of bisphenol-A. The second step was the cyclization using the syringe pump technique to maintain the high dilution condition. The pure macrocycle was obtained by column chromatography in 11 % yield. The cyclic dimer is highly crystalline and has a melting point of 505 °C. Its X-ray structure has recently been resolved by Colquhoun and Williams.⁴¹ This macrocycle is approximately rectangular in shape and adopts a very rigid conformation and has a very open cavity. The high melting point of this macrocycle can be attributed to its high rigidity. Unfortunately, its high melting point prevents it from ring-opening polymerization.

[40] Ganguly, S.; Gibson, H. W. *Macromolecules* **1993**, 26, 2408.

[41] Colquhoun, H. M.; Williams, D. J. *Macromolecules* **1996**, 29, 3311.

Scheme 1.16



Ar	Cyclic Yield (%)
	80 (R=H)
	90 (R=H) 90 (R=Ph)
	90 (R=H) 90 (R=Ph)
	80 (R=H) 80 (R=Ph)
	95 (R=H)
	70 (R=Ph)

More recently, Hay's group has been actively involved in study of the synthesis and ring-opening polymerization of macrocyclic monomers. In 1995, they reported high yield syntheses of cyclic arylene ether ketones mixtures first in the preliminary form⁴² followed by more detailed studies.⁴³ Their first system involved fluoroketone monomers containing 1,2-dibenzoylbenzene units (Scheme 1.16). They used the well known pseudo-high dilution principle to get a number of macrocyclic mixtures with yields ranging from 70-95 %. The cyclics were simply purified by precipitating the solution of the crude product into methanol. Their procedure was similar to what Gibson's group had reported. Monomers were added to a solvent reservoir suspension of potassium carbonate over a period of 8 hours. The final concentration of the product was as high as 40 mM. Toluene was used as an azeotropic solvent to remove water. The amount of toluene was kept minimal to increase the rate of reaction. The reaction was complete within another 8 hours. If cesium carbonate was used instead of potassium carbonate, the reaction time was cut in half. They found that monomer structures have significant effect on the final cyclic yields. Using the rigid and orthogonal spirobiindane group gave better yields and high reaction concentration can be tolerated. They also found that some dipolar aprotic solvents such as N, N-dimethylacetamide, N-methyl-2-pyrrolidinone and dimethyl sulfoxide were not appropriate for this type of cyclization reaction. They

[42] Chan, K. P.; Wang, Y-F.; Hay, A. S. *Macromolecules* **1995**, *28*, 653.

[43] Chan, K. P.; Wang, Y-F.; Hay, A. S.; Hronowski, X. L.; Cotter, R. J. *Macromolecules* **1995**, *28*, 6705.

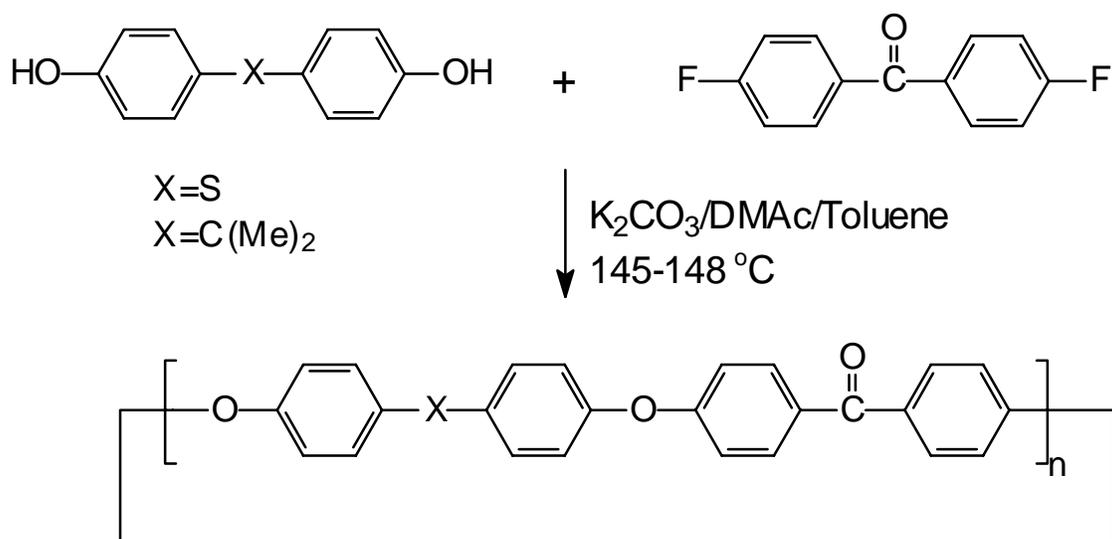
suggested that DMF is the best solvent. When DMAc was used an enamine aldol condensation reaction occurred. This side reaction was detected by ^1H NMR and MALDI-TOF-MS. Various techniques were applied to prove the formation of the cyclic structures. Gel permeation chromatography (GPC) showed that the mixtures were of low molecular weight nature, with an average of about three repeating units. ^{13}C and ^{19}F NMR spectra showed no obvious terminal groups. The amount of fluoro terminal groups was determined to be one in every 300 repeating units. These results were further confirmed by MALDI-TOF-MS. It was found that using 1, 8, 9-anthracenetriol as matrix and $\text{CF}_3\text{CO}_2\text{Ag}$ as cationization agent gave better signal/noise ratio. Up to octamer (molecular weight around 5000) can be detected. The calculated molecular weights of the cyclics matched the experimentally determined values within the experimental errors. The size distributions of the cyclics were obtained by reverse phase HPLC and GPC analyses. Using a gradient solvent of THF and H_2O , cyclic oligomers up to 10 repeating units can be detected. ^{13}C NMR can also detect cyclic oligomers as high as 5 repeating units. They fit their cyclic distribution data to the Jacobson and Stockmayer (JS theory) equation. It was found that the experimentally determined γ value is very close to the predicted value of 2.5.

They also studied the thermal properties of their macrocyclic mixtures. Most of the cyclic oligomers are crystalline. Glass transition temperatures of the cyclic oligomers are generally 10-20 $^\circ\text{C}$ lower than the corresponding linear

oligomers. They attributed the crystalline nature of the mixtures to the large amount of cyclic dimer present.

In some cases, the melting point of a cyclic mixture is too high to be practical for ring-opening polymerization. They came up with the idea of making comacrocyclus to reduce the melting point. In this approach, one monomer (difluoroketone) was cyclized with two different bisphenols simultaneously to get a mixture of different macrocycles containing various numbers of different repeating units. Most of the comacrocyclus mixtures made by this method thus are amorphous.

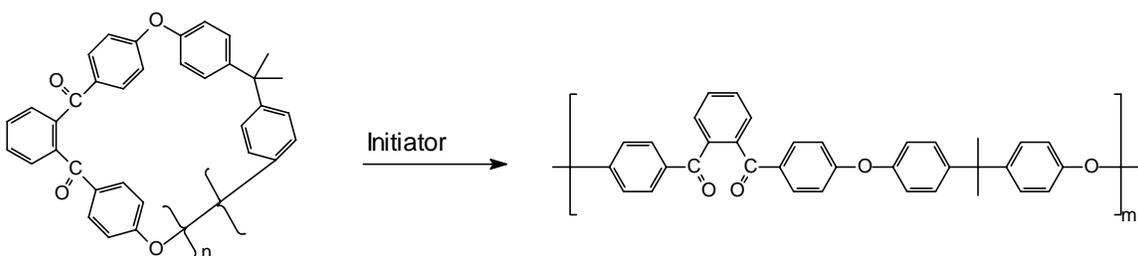
Scheme 1.17



They extended their work by making a number of other macrocycles based upon 4,4'-difluorobenzophenone (Scheme 1.17). Similar results such as yields and size distribution were obtained.

Hay's group reported similar work with macrocyclic aryl ethers containing the tetraphenylbenzene moiety.⁴⁴ The experimental conditions were slightly different. The difluoroketone monomer is not soluble in the solvent at room temperature, so they added the monomer in portions without using a syringe pump. The reactants were delivered in 10 portions over a period of 9 hours. In this work, more experiments were performed to prove the cyclic nature of the mixture in addition to the standard analytical techniques (NMR, MALDI-TOF). Linear oligomers, which have molecular weights similar to the cyclic mixture were synthesized. HPLC chromatograms of the two were compared. HPLC indicated that there were no detectable linear oligomers present in the mixtures. The cyclic mixtures have either very high melting points or high T_g 's. No ring-opening polymerization study has been performed on these macrocycles.

Scheme 1.18



The ring-opening polymerization studies of macrocyclic mixtures based upon 1, 2-dibenzoylbenzene bisphenol-A ether from Hay's group appeared in 1996⁴⁵ (Scheme 1.18). By far, this has been the most detailed report of the ring-

[44] Ding, Y.; Hay, A. S. *Macromolecules* **1996**, 29, 3090.

[45] Wang, Y-F; Chan, K. P.; Hay, A. S. *J. Polym. Sci.: Part A: Polym. Chem.* **1996**, 34, 375.

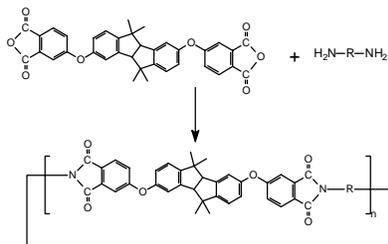
opening polymerization of this type of monomers. Various initiators such as CsF, cesium, potassium and sodium phenolates were used in their study. The first thing noticed was the large amount of gel formed in the melt ring-opening polymerization. Polymerization with 1 mol % CsF at 300 °C for 30 minutes gave a high molecular weight polymer and 37 % gel. The best initiator system they found was potassium 4,4'-bisphenoxide, which afforded high molecular weight polymers with high conversion (98 %). Comparing different metallic phenoxides, the order of reactivity is K>Cs>Na in the melt, while it is K>Cs>Na in solution.

C. Cyclic Oligomeric Ether imides

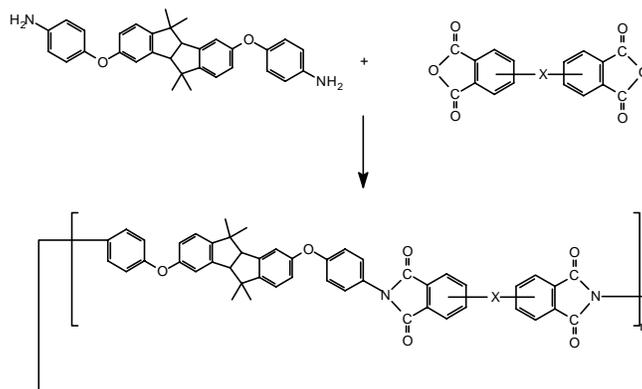
Extension of Brunelle's cyclic polycarbonate work resulted in the syntheses of cyclic ether imides by researchers at GE.⁴⁶ The formation of cyclic oligomeric ether imides was carried out by the reaction of dianhydrides and various diamines (Scheme 1.19) in o-dichlorobenzene using standard imidization techniques. The reaction concentrations were between 0.01-0.05 M. Again, the spirobiindane groups contribute to the tendency for cyclization. The cyclic yields were from fair to excellent (25 % vs 77 %).

[46] Cella, J. A.; Fukuyama, J.; Guggenheim, T. L. *Am. Chem. Soc. Div. Polym. Chem. Polym. Prepr.* **1989**, 30(2), 142.

Scheme 1.19



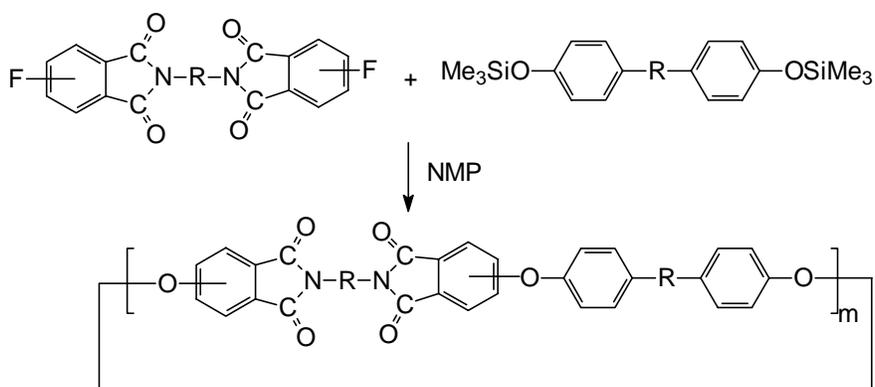
R	Cyclics Yield (%)
	60
	77
	50
	25
	64



X	Cyclics Yield (%)
-O- (4,4)	40
-O- (3,3)	30
-S- (4,4)	40
-S- (3,3)	75
	45
	40

Attempts to ring-opening polymerize these macrocycles by either imide or ether exchange processes were not successful. The imide exchange induced by catalytic amounts of amine was very slow in DMAc at 200 °C. The more feasible route is using the ether exchange reaction. The cyclic oligomers obtained from spirodiamine are insoluble and can not be ring-opening polymerized either in solution or in the melt (mp too high). Some soluble cyclic polyimides were ring-opening polymerized in DMAc with sodium sulfide. GPC indicated that although high molecular weight polymer ($M_w=140$ kg/mol) was obtained, there was a substantial amount of unpolymerized cyclics. The resulting polymer film was brittle.

Scheme 1.20



Takekoshi and Terry⁴⁸ recently reported synthesis of macrocyclic oligoimides via Kricheldorf's substitution polymerization (Scheme 1.20), which involves polycondensation of bis(trimethyl silyl) ethers of bisphenols and various

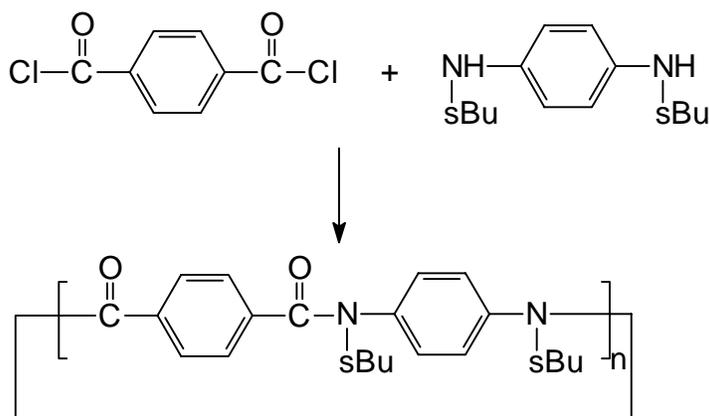
[48] Takekoshi, T.; Terry, J. M. *J. Polym. Sci.: Part A: Polym. Chem. Ed.* **1997**,

35, 759.

bis(fluorophthalimide)s. The cyclic yields were around 70 %. These cyclics were characterized by HPLC and field-desorption MS. They found the cyclics are more soluble than the linear polymers. No thermal properties were reported and no ring-opening polymerization was mentioned.

D. Macrocylic polyamides

Scheme 1.21



There has been an excellent review of macrocyclic polyamide systems by Memeger.⁴⁹ Macrocylic polyamides are generally very difficult to make because the trans conformation of the amide group is unfavorable for the cyclization reaction. Memeger⁵⁰ and coworkers at DuPont found that N-alkyl substituted cyclic polyamides were formed readily under high dilution conditions (Scheme 1.21). Cyclic yields up to 85 % yield were obtained. The propensity for formation of the cyclics is mainly due to the N-substituted alkyl which probably

[49] Memeger, W., Jr. in "Polymeric Materials Encyclopedia", Salamone, J. C. Ed., CRC Press, NY, **1996**, Vol 6., 3873.

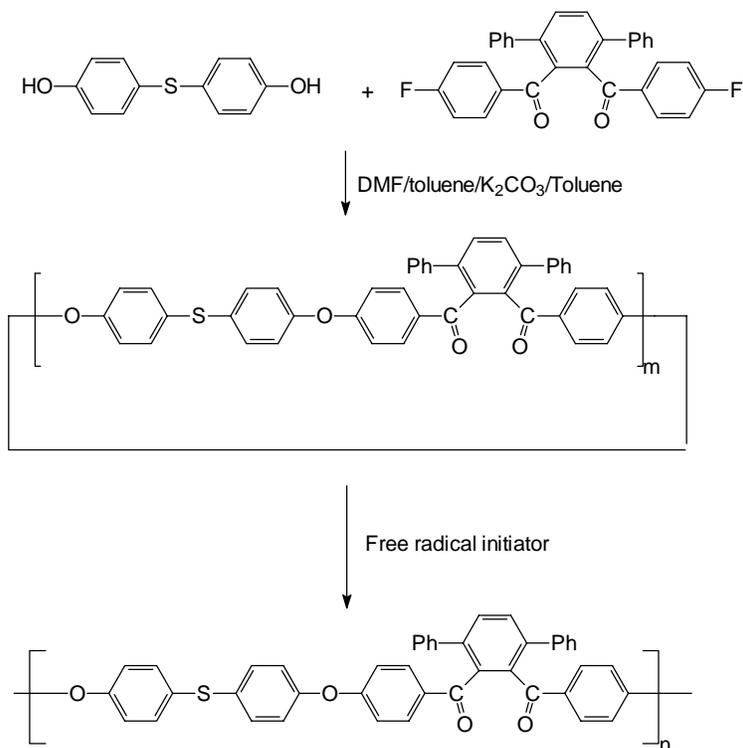
[50] Memeger, W. Jr.; Lazar, J.; Ovenall, D. J.; Arduengo, A. J., III; Leach, R. A. *Macromol. Symp.* **1994**, 77, 43.

favors the cis conformation of the amide groups. These cyclic mixtures can be ring-opening polymerized with nucleophilic initiators such as 1,3-dialkylimidazole-2-thiones to give moderate molecular weight polyamides but conversion was not complete. Using an acidic cocatalyst resulted in complete conversion, but also some N-dealkylation.

E. Macrocyclic Monomers Containing Thioether Linkages

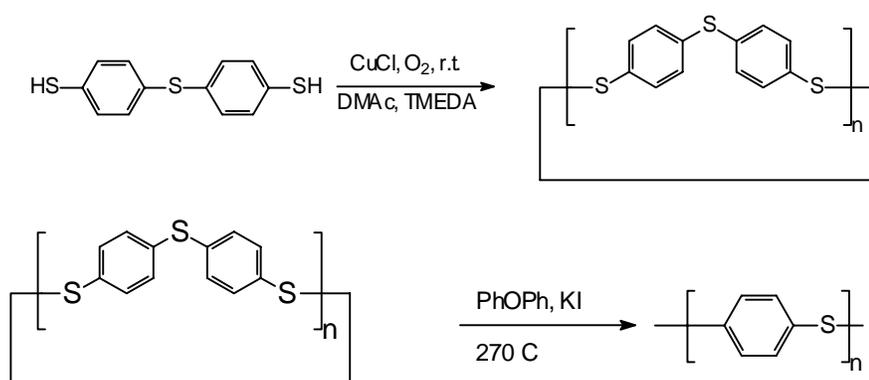
More recently the interest of Hay's group has been shifted to cyclic monomers containing thioether linkages. They made a very interesting discovery that the macrocyclic monomers containing thioether linkages can be ring-opening polymerized via a free radical mechanism with initiators such as sulfur.

Scheme 1.22



In their first method, the macrocycle containing the thioether linkage was pre-made in the monomer.⁵¹ The macrocyclic mixture was synthesized by S_NAr cyclization (Scheme 1.22). It was found that in the absence of an initiator, the cyclic was ring-opening polymerized when heated at 380 °C for 30 minutes with about 77 % conversion. The free radical mechanism was confirmed by ESR experiments. It is believed that the C-S bond undergoes homolytic cleavage to form the thio-radical under heat. With some added free radical initiator the conversion can be pushed to near completion and formation of high molecular weight polymers was detected by GPC.

Scheme 1.23



In their second method, an aromatic cyclic polythioether (Scheme 1.23) was synthesized from 4,4'-thiobis(benzenethiol) with oxygen using copper-amine catalysts under high dilution conditions.⁵² DMAc was found to be the best solvent. The final concentration was as high as 0.05 mM. GPC showed the

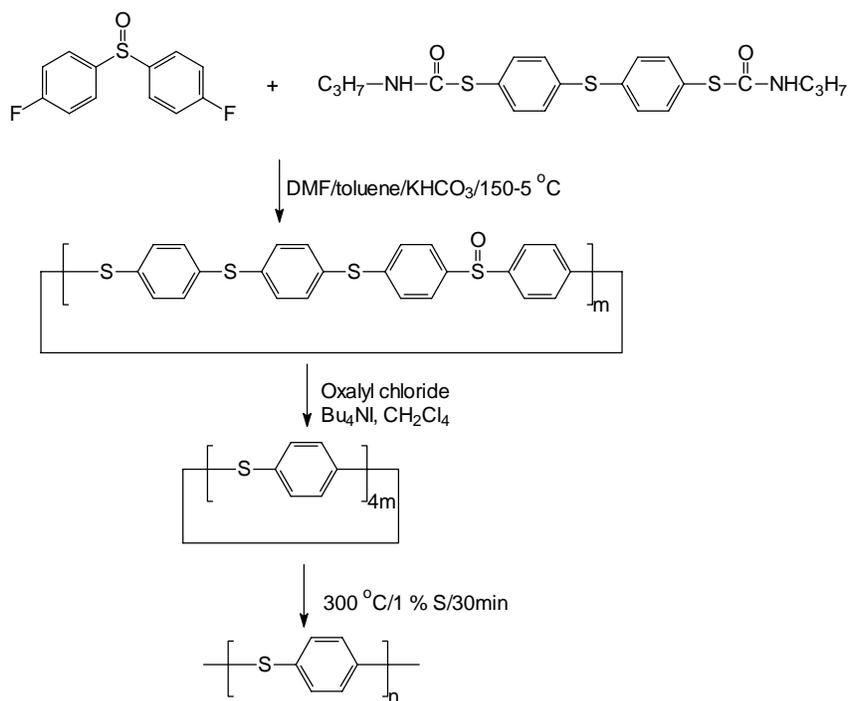
[51] Wang, Y-F; Chan, K. P.; Hay, A. S. *Macromolecules* **1996**, 29, 3717.

[52] Ding, Y.; Hay, A. S. *Macromolecules* **1996**, 29, 4811.

molecular weight of the cyclic mixture was very low. ($M_n=380$, $M_w=570$). This macrocyclic mixture was ring-opening polymerized with about one equivalent of 1,4-dihalobenzene in diphenyl ether solution to give the poly(p-phenylene sulfide) in 95 % yield. The formation of high molecular weight polymer was detected by the glass transition temperature and the melting point of the final polymer, which are comparable with the values of polymer obtained from other synthetic methods. Solid state ^{13}C NMR also confirmed the structure.

A number of other thioether containing aromatic macrocycles⁵³ were similarly synthesized with a range of cyclic yields from 74 to 99 %. But no ring-opening polymerization of these monomers was reported.

Scheme 1.24



[53] Ding, Y.; Hay, A. S. *Macromolecules* **1996**, 29, 6386.

In their third method, sulfoxide was transformed into the thioether.⁵⁴ First the macrocyclic mixture was synthesized by the S_NAr method (Scheme 1.24). Then sulfoxide was reduced to thioether. The cyclic thioether was polymerized with 1 mol % elemental sulfur to form a tough and flexible polymer with a melting point of 275 °C.

1.4 Applications of the Macrocyclic Monomer Technique

The potential areas of application of macrocyclic monomers include matrix materials for composites, structural adhesives and reactive injection molding materials. Two techniques have been disclosed by GE researchers⁵⁵ for the bisphenol-A based polycarbonate system. One is pultrusion, in which, a continuous glass fiber was coated with initiator by passing through an initiator bath. After being dried in an oven, the strands passed through a die into which molten cyclic monomer was continuously injected. The coated cyclics were polymerized in an oven to form rigid rods of polycarbonate/glass composite. In the resin transfer molding process, the cyclics were melted and mixed with the initiator and then rapidly injected into a closed mold containing the fibrous support. The low viscosity of the cyclics allowed large volumes of cyclics to be moved with only very little pressure (ca. 50 psi). Although some voids were formed in the process, consolidation of the finished part by compression at 690

[54] Wang, Y-F; Hay, A. S. *Macromolecules* **1996**, 29, 5050.

[55] Brunelle, D. J. *Am. Chem. Soc. Div. Polym. Chem. Polym. Prepr.* **1996**, 37(2), 698.

psi at 300 °C gave void-free parts with up to 72 % glass support. No mechanical properties were reported. In their US patent, Mullins and coworkers⁵⁶ at Dow Chemical demonstrated the fabrication of composite materials using the cyclic poly(ether sulfone) mixture. In one example, the cyclics were ring-opening polymerized with 0.5 % of CsF in a mold containing 65-35 % carbon fiber under pressure to get a composite panel. MacKnight's group⁵⁷ reported *in situ* polymerization of cyclic bisphenol-A carbonate oligomers in a miscible blend with a styrene-acrylonitrile copolymer. They found that after the ring-opening polymerization of the cyclics the final material had morphologies unattainable via conventional melt blending. Very fine phase dispersion of the polycarbonate phase was achieved by this method and increased ductility of the blend was observed.

1.5 Summary of Literature Work on the Macrocyclic Monomers

Following Brunelle's work on polycarbonate, it has been recognized that macrocyclic monomers for condensation polymers can be conveniently synthesized under pseudo-high dilution conditions. However, in many cases the melting points of the cyclic mixtures are too high for practical ring-opening polymerization. Despite the large amount of work in this area, the structure-property relationships of these relatively new materials are not evident. In addition, there is a lack of systematic study of the ring-opening polymerization of

[56] Mullins, M. J. Woo, E. P. US Patent 5,264,520 (1993).

[57] Nachlis, W. L.; Kambour, R. P.; MacKnight, W. J. *Polymer* **1994**, 17, 3643.

cyclic ether ketone or sulfone monomers. The ring-opening polymerization is not very successful and particularly complete conversion of the monomers is very difficult to achieve. Another phenomenon is that the polymers generated by the macrocyclic monomer technique are generally amorphous. There has been no report of ring-opening polymerization of macrocycles for the more valuable semicrystalline poly(ether ketone). These problems will be addressed in our work, which is described in later chapters.

Chapter 2

Synthesis and Characterization of Macrocyclic Monomers Based on Bisphenol-A and 4,4'-Difluorobenzophenone

2.1 Introduction

As discussed in Chapter 1, cyclic poly(ether ketone) or sulfone mixtures can now be conveniently synthesized from bisphenols and activated dihalides via nucleophilic aromatic substitution reaction under pseudo-high dilution conditions.¹⁻⁷ However, it can not be avoided that the cyclic mixtures are somehow contaminated by linear oligomers. The presence of linear oligomers with reactive terminal functional groups such as fluoroketones or phenols can

[1] Fukuyama, J. M.; Talley, J. J.; Cella, J. A. *Poly. Prepr. Am. Chem. Soc., Div. Polym. Chem.* **1989**, 30 (2), 174.

[2] Mullins, M. J.; Galvan, R.; Bishop, M. T.; Woo, E. P.; Gorman, D. B.; Chamberlin, T. A. *Poly. Prepr. Am. Chem. Soc., Div. Polym. Chem.* **1991**, 32(2), 174.

[3] Mullins, M. J.; Woo, E. P. US Patent 5, 264, 520 (**1993**).

[4] Ganguly, S.; Gibson, H. W. *Macromolecules* **1993**, 26, 2408.

[5] Chan, K. P.; Wang, Y. F.; Hay, A. S. *Macromolecules* **1995**, 28, 653.

[6] Chan, K. P.; Wang, Y. F.; Hay, A. S.; X. L. Hronowski; Cotter, R. J. *Macromolecules* **1995**, 28, 6705

[7] Ding, Y.; Hay, A. S. *Macromolecules* **1996**, 29, 3090.

complicate the ring-opening polymerization. We are interested in synthesizing pure single sized macrocycles, especially the dimer, to facilitate the ring-opening polymerization study. From the material processing point of view, the melting point of a cyclic mixture is important. The cyclic dimer, which has the highest melting point, dictates the melting of a cyclic mixture. Systematic study of the structure-property relationships of the dimer is useful to get insight of the behaviors of the cyclic mixtures. We are also interested in using these aromatic macrocycles as cyclic components for the synthesis of polyrotaxanes.⁸ The cavities⁹ of these relatively rigid macrocycles are more open than their aliphatic analog, i. e., crown ethers. These types of cyclics are also expected to have high thermal stability.

In the synthesis of the macrocyclic compounds, one piece, two piece or multiple piece cyclization can be used. From the entropic point of view, cyclization is unfavorable using the multiple piece method. In a previous study, a two piece cyclization reaction method using an extended bisphenol was reported from our lab. However, it is very difficult to get the extended bisphenol with high purity, which is necessary to maintain the correct stoichiometry in the cyclization step. Therefore, we designed a protection-deprotection approach to

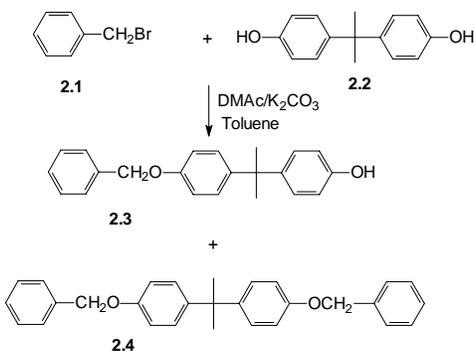
[8] (a) Gibson, H. W.; Bheda, M. C.; Engen P. T. *Prog. Polym. Sci.* **1994**, 19, 843. (b) Gong, C.; Gibson, H. W. Polyrotaxanes and Related Structures: Synthesis and Properties, *Curr. Opin. Solid St. Mater. Sci.*, **1998**, 2, submitted. July 30, 1997.

[9] Colquhoun, H. M.; Williams, D. J. *Macromolecules* **1996**, 29, 3311.

get the extended bisphenol in high purity. The first system using this approach is based upon bisphenol-A and 4,4'-difluorobenzophenone.

2.2 Synthesis of Extended Bisphenol Precursor

Scheme 2.1



The first reaction is the protection of bisphenol-A with benzyl bromide under homogeneous reaction conditions (**Scheme 2.1**). The reaction was carried out in a dipolar solvent, dimethylacetamide (DMAc). Toluene was used as an azeotropic solvent to remove water from the system in order to avoid hydrolysis of the benzyl bromide. The reaction was very fast. As soon as benzyl bromide was added salt formed from the reaction was observed. One problem is the formation of the dibenzyl ether of bisphenol-A (DBEB), which can not be easily separated from the desired product. TLC showed that there were three compounds in the crude product, i. e., unreacted bisphenol-A, the monobenzyl ether of bisphenol-A and DBEB. Excess bisphenol-A can be easily removed by treating the mixture with aqueous NaOH or KOH. The separation of the monobenzyl ether and DBBE made use of their solubility difference in methanol. The DBBE is only slight soluble in methanol, while the desired

product is quite soluble in methanol. The final product was further purified by recrystallization from hexanes/1-hexanol.

Table 2.1 The yield of monobenzyl ether of bisphenol-A as related to the reaction conditions

Trial	Temperature (oil bath °C)	Stirring	Stoichiometric Ratio	Purification Procedure	Yield (%)
1	180-200	magnetic	5:1	A	33
2	180-200	magnetic	5:1	B	48
3	100-120	mechanical	5:1	B	68
4	100-120	mechanical	1.5:1	C	38

Stoichiometric ratio: bisphenol-A/benzyl bromide. For purification procedures see details in the experimental part.

Table 2.1 lists the yields as related to the reaction conditions. Obviously the larger the excess of bisphenol-A, the less the amount of DBBE. Therefore, 50-400 % excess bisphenol-A was used. Only 50 % excess of bisphenol-A was used in trial 4. So the yield was significantly lower, but the yield per gram of bisphenol-A was higher. Trial 3 gave the highest yield because of better mechanical stirring and low reaction temperature, so that benzyl bromide was well dispersed before the reaction took place.

Later on it was found that researchers at General Electric had developed a novel method to synthesize the same compound.¹⁰ In this method, bisphenol-A was first dissolved in aqueous KOH and then benzyl bromide was added under vigorous agitation. The product was formed within several minutes. The

[10] Humphrey, Jr., J. S.; Shultz, A. R. and Jaquiss D. B. G. *Macromolecules* **1973**, 6, 305.

desired product precipitated out from the suspension, thus preventing further reaction to form the dibenzyl ether. Vigorous agitation is necessary to disperse the benzyl bromide into small droplets in order to prevent the side reaction. The reaction is believed to take place between the interface of benzyl bromide and the aqueous solution. Excess bisphenol-A potassium salt is soluble in the aqueous solution and can be removed by filtration. In this method, very little DBBE was found as indicated by TLC. The yield was 60 %.

The structure of **2.3** was confirmed by IR and ^1H NMR spectroscopies. In its IR spectrum (Figure 2.1), the OH group is located at 3216 cm^{-1} and the peak corresponding to the ether group appears at 1233 cm^{-1} . In the 400 MHz ^1H NMR spectrum (Figure 2.2), the CH_2 and OH groups are singlets located at 5.03 and 4.71 ppm, respectively. The multiple peaks around 7.4 ppm are due to the benzyl phenyl group. The remaining peaks are four doublets, which are assigned according to the ^1H - ^1H dqcosy spectrum.

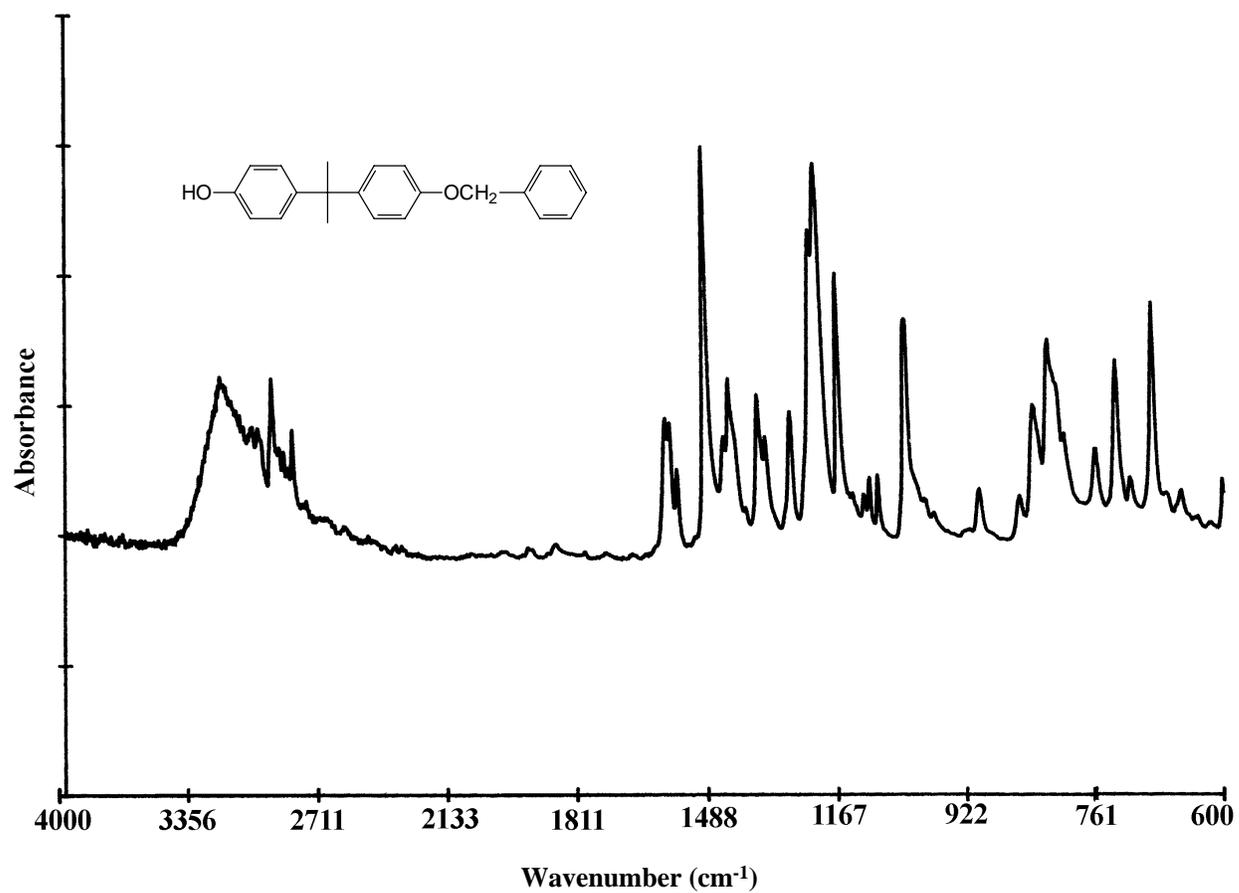


Figure 2.1. IR spectrum of monobenzyl ether of bisphenol-A (KBr pellet).

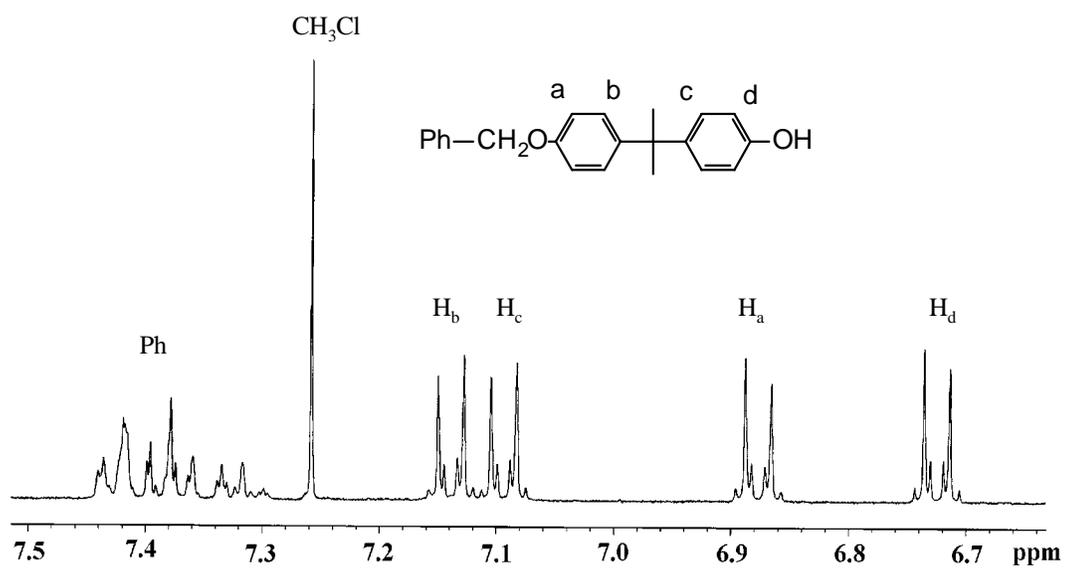
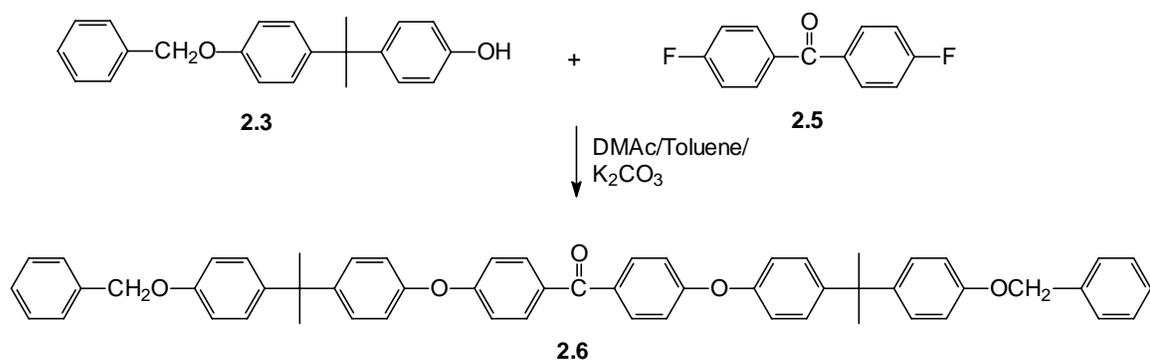


Figure 2.2. 400 ^1H NMR spectrum of monobenzyl ether of bisphenol-A in CDCl_3 .

The melting point of **2.3** is 109.7-111.1 °C , which is higher than the reported value (107-108 °C). One spot on TLC, narrow melting point and absence of impurity peaks in the NMR spectrum indicate very pure **2.3** was obtained. The high purity is necessary for the next reaction.

Scheme 2.2



The next step is a typical nucleophilic aromatic substitution (S_NAr) reaction involving the monoprotected bisphenol-A and 4,4'-difluorobenzophenone (Scheme 2.2). The reaction was carried out in DMAc, a typical S_NAr solvent. Again toluene was used as the azeotropic solvent and potassium carbonate was used as the base. The new compound **2.6** was obtained in almost quantitative yield. The reaction time and temperature are two factors to be considered for this reaction. In the first trial the reaction time was only 4 hours and reaction temperature was 150-160 °C (oil bath). TLC showed that the reaction was incomplete and the yield was poor (58 %). In the subsequent trials the temperature was maintained at reflux and the reaction time was extended to 24 hours. TLC indicated that there was only one spot from the product and no detectable impurity peak in the NMR spectrum. Therefore, no further purification

was performed other than washing the product with methanol. The melting point of this compound is 94.4-95.8 °C. The yield was close to quantitative (98 %). Purer white product was obtained by recrystallization in a mixed solvent of hexanes/ethyl acetate for elemental analysis. Elemental analysis results agree well with its formula within the experimental error. The IR spectrum (Figure 2.3) of **2.6** indicates the disappearance of the OH group from the starting material. The carbonyl and the ether groups are located at 1652 and 1241 cm^{-1} respectively. In the ^1H - ^1H COSY NMR spectrum (Figure 2.4), protons H_a adjacent to the electron withdrawing carbonyl group are located at 7.78 ppm. They are coupled with protons H_b . Protons ($\text{H}_b, \text{H}_c, \text{H}_f$) ortho to the ether linkages are located upfield. H_c and H_f are coupled with H_d, H_e respectively. All these are consistent with the structure. Compound **2.6** is soluble in common organic solvents such as acetone, acetonitrile, chloroform, ethyl acetate, etc.

The next step is the removal of the protecting benzyl ether groups from compound **2.6**. The most common and convenient method is Pd/C catalyzed hydrogenolysis. Normally hydrogenolysis is a clean reaction and the byproduct is toluene, which can be easily removed. The reaction was carried out in ethyl acetate. After 85 hours of reaction, TLC indicated that the starting material had disappeared and two products were obtained. The major product (top spot) was isolated by column chromatography. This product was analyzed with NMR and

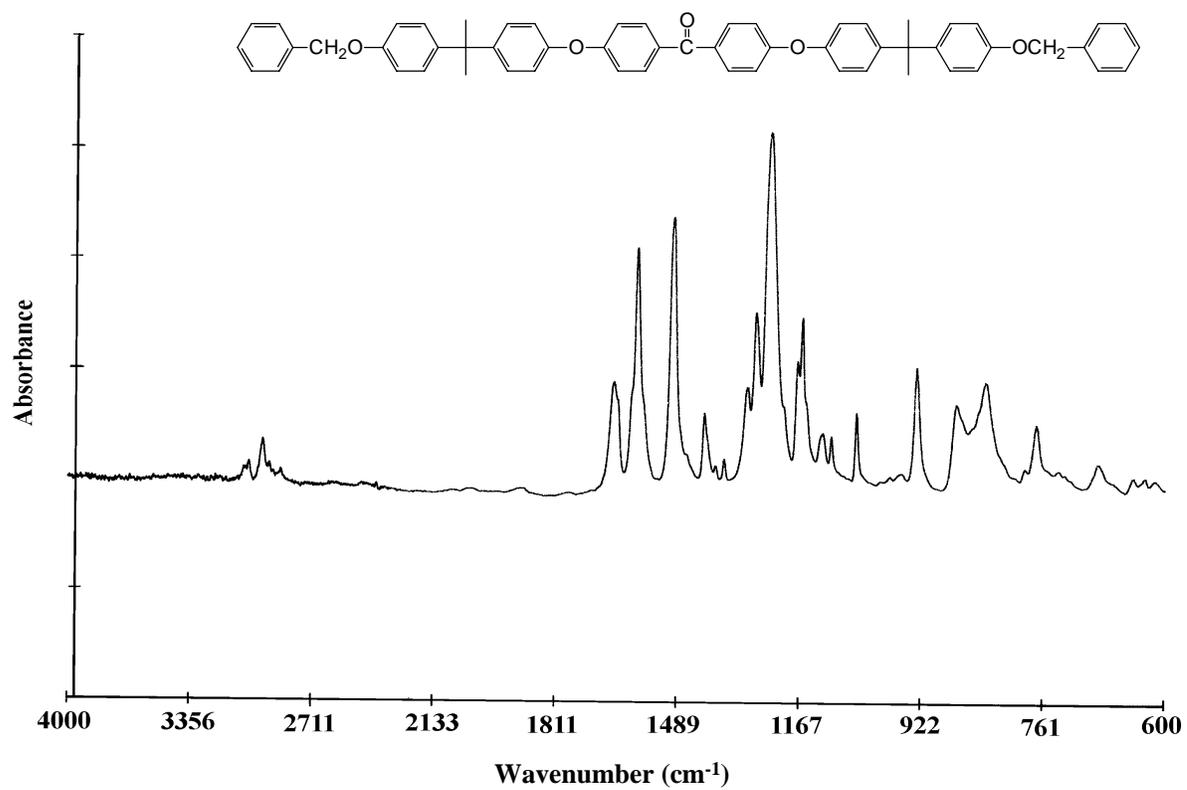


Figure 2.3. IR spectrum of compound **2.6** (KBr pellet).

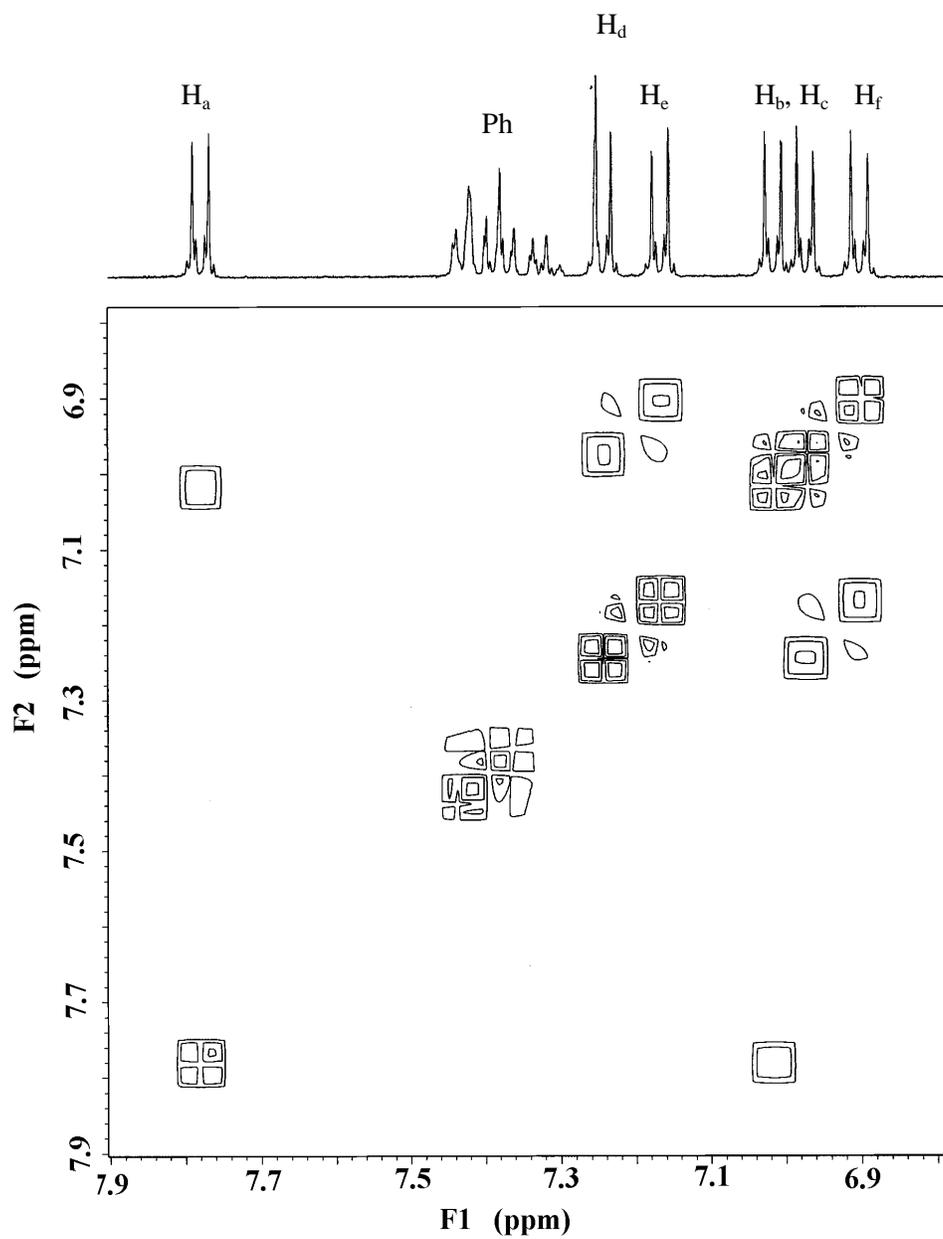
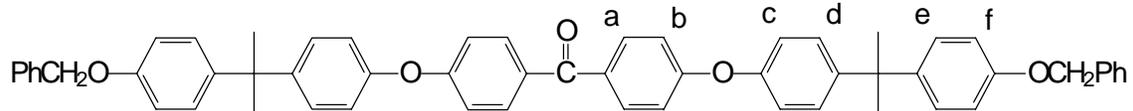


Figure 2.4. 400 MHz ¹H-¹H COSY spectrum of compound **2.6** in CDCl₃.

IR. The IR spectrum indicated that the benzyl group was removed. There was a broad OH absorption at 3343 cm^{-1} . But the carbonyl peak expected around 1650 cm^{-1} disappeared, which suggested that the carbonyl was also reduced during the hydrogenolysis process. NMR analysis of the product confirmed that the benzyl group was indeed removed. The benzyl phenyl peaks at $\delta=7.4$ ppm disappeared. The absence of the doublet at $\delta=7.78$ ppm suggested that the electron withdrawing carbonyl group had also gone. The carbonyl group can be reduced to either hydroxyl or a CH_2 group.¹¹ Based on the fact that the integral of CH_2 signal is the same as that of OH signal, it can be concluded that the carbonyl was transformed to a CH_2 group. Therefore, it is impossible to retain the carbonyl group while removing the benzyl group by the convenient hydrogenolysis method.

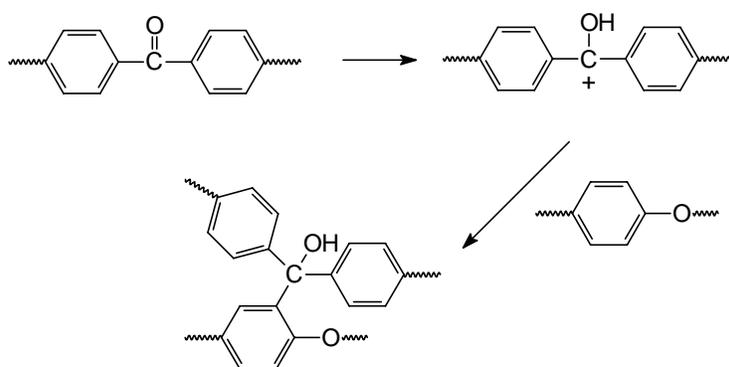
In addition to the hydrogenolysis method, there are a number of other ways available to remove the benzyl ether group. These methods have been thoroughly reviewed by Bhatt and Kulkarni.¹² Treating **2.6** with trifluoroacetic acid gave a very complicated mixture as shown by TLC, although it was reported that trifluoroacetic acid was a selective benzyl ether cleavage reagent.¹³ The NMR spectrum of the crude product indicated that the benzyl group was indeed removed. Formation of the complicated products is probably due to the

[11] Carey, F. A.; Sundberg, R. J. *Advanced Organic Chemistry, Part B: Reactions and Synthesis*, 3rd Ed. Plenum Press, New York, **1990**.

[12] Bhatt, M. V.; Kulkarni, S. U. *Synthesis* **1983**, 249.

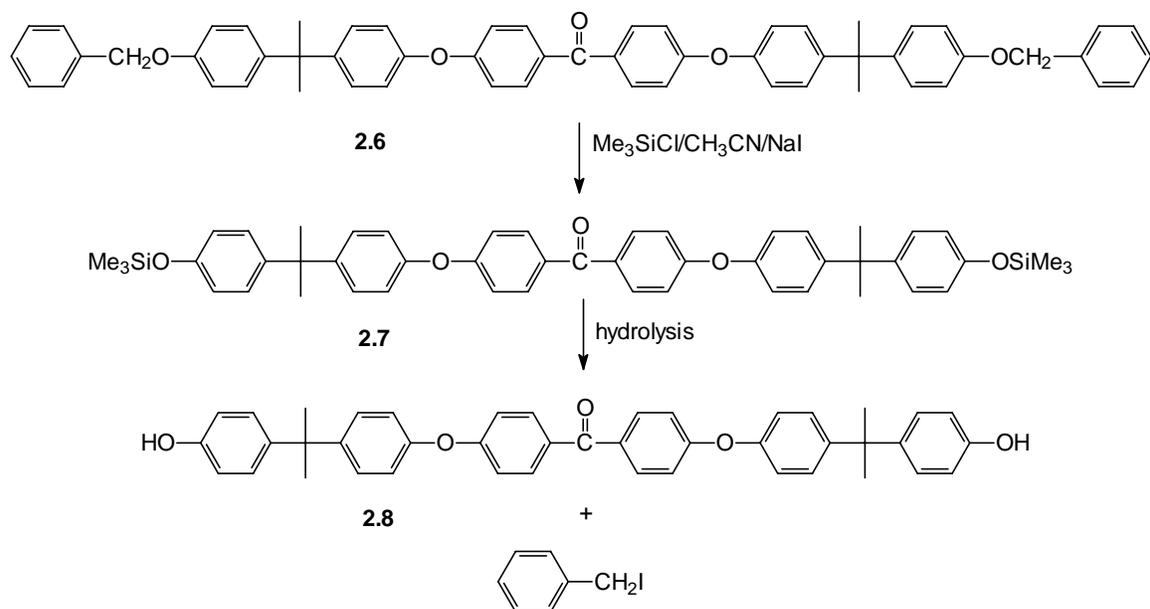
carbonyl group. The carbonyl group can be protonated by the strong acid and participate in the electrophilic Friedel-Crafts substitution reaction (Scheme 2.3). A complicated mixture of products is not unexpected if we consider that there are multiple substitution sites. Using concentrated HCl did not give the desired product either probably for the same reason.

Scheme 2.3



[13] March, Jr. J. P.; Goodman, L. J. *J. Org. Chem.* **1965**, 30, 1491.

Scheme 2.4



Olah et al. have developed a general ether cleavage method using trimethylsilyl chloride and sodium iodide reagents.¹⁴ The successful debenzylation reaction using Olah's reagents is outlined in Scheme 2.4. It was carried out in refluxing acetonitrile following procedures similar to those reported in the literature.¹⁴ In this reaction, the more reactive but less stable trimethylsilyl iodide was generated in situ by the exchange reaction. As soon as the trimethylsilyl chloride was added, a precipitate of sodium chloride was observed. The reaction was quite slow. In the first trial, the reaction time was about 9 hours. The reaction was incomplete and product was isolated by column

[14] Olah, G. A.; Narang, S. C.; Gupta, B. G. B.; Malhotra *J. Org. Chem.* **1979**, 1247.

chromatogram in 62 % yield. It took about 30 hours for the reaction to complete even in a large excess of the trimethylsilyl chloride. The yield increased to 86 % after prolonged reaction. The product was purified by column chromatography. A more convenient purification method is exhaustive extraction of crude product in acetonitrile solution with hexanes to remove the benzyl iodide byproduct.

Compound **2.8** was characterized by IR, ^1H NMR and elemental analysis. The IR spectrum shown in Figure 2.5 indicates the presence of OH (3389 cm^{-1}), ketone (1636 cm^{-1}) and ether (1244 cm^{-1}) groups. The ^1H - ^1H COSY NMR spectrum in the aromatic region is shown in Figure 2.6. The benzyl signal has disappeared. There are four pairs of doublets coupled with each other. These doublets are assigned based upon the correlation pattern and the known positions of protons ortho to the carbonyl and OH groups. Elemental analysis results agree well with the calculated values, indicating a pure compound was obtained. The compound looks like a glassy material and gives a broad melting point ($89\text{-}94\text{ }^\circ\text{C}$) due to its inability to crystallize well because of the kinked conformation caused by the isopropylidene units.

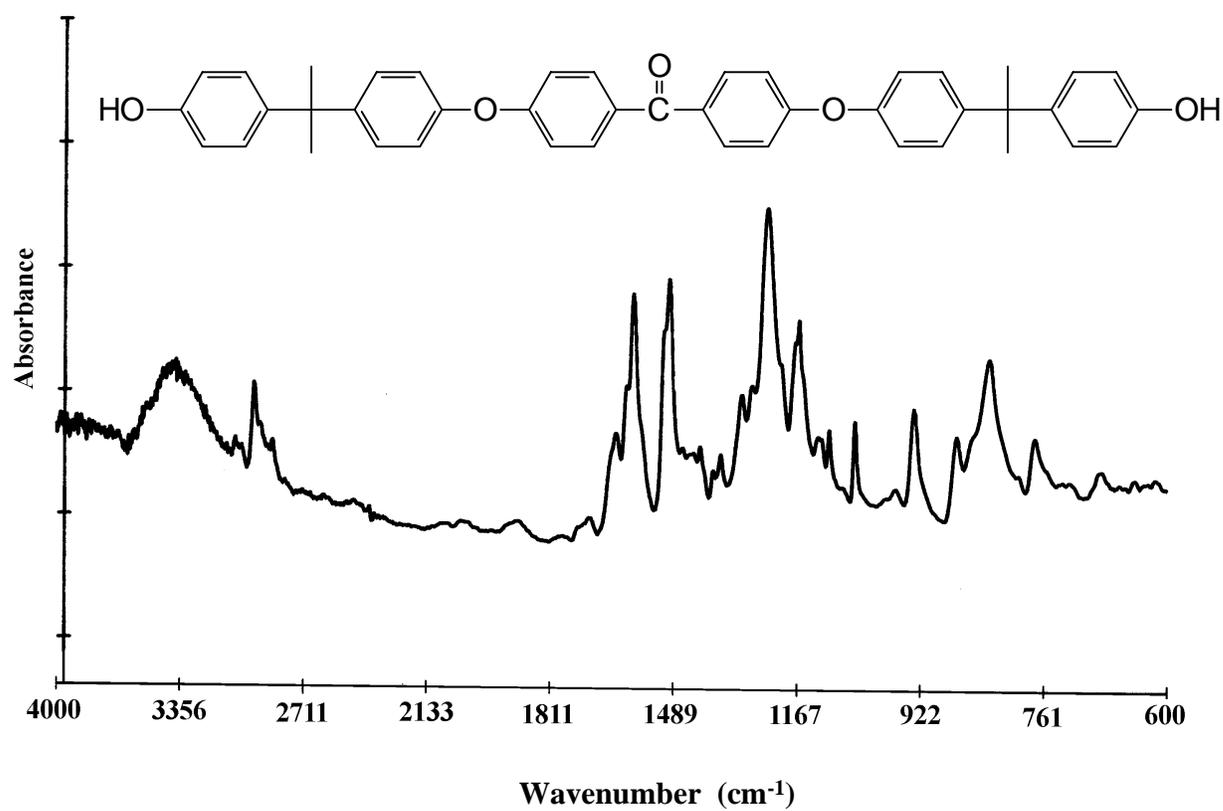


Figure 2.5 IR spectrum of compound 2.8 (KBr pellet).

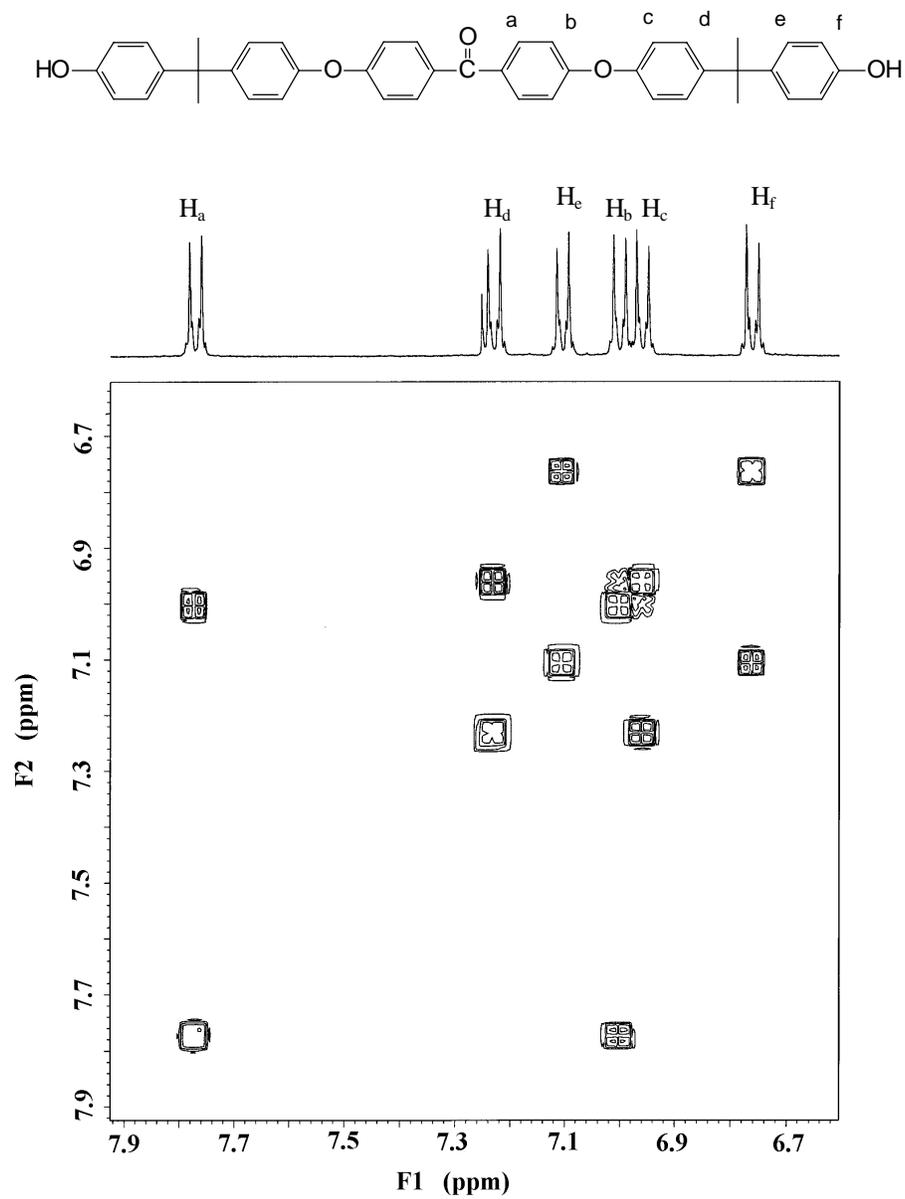
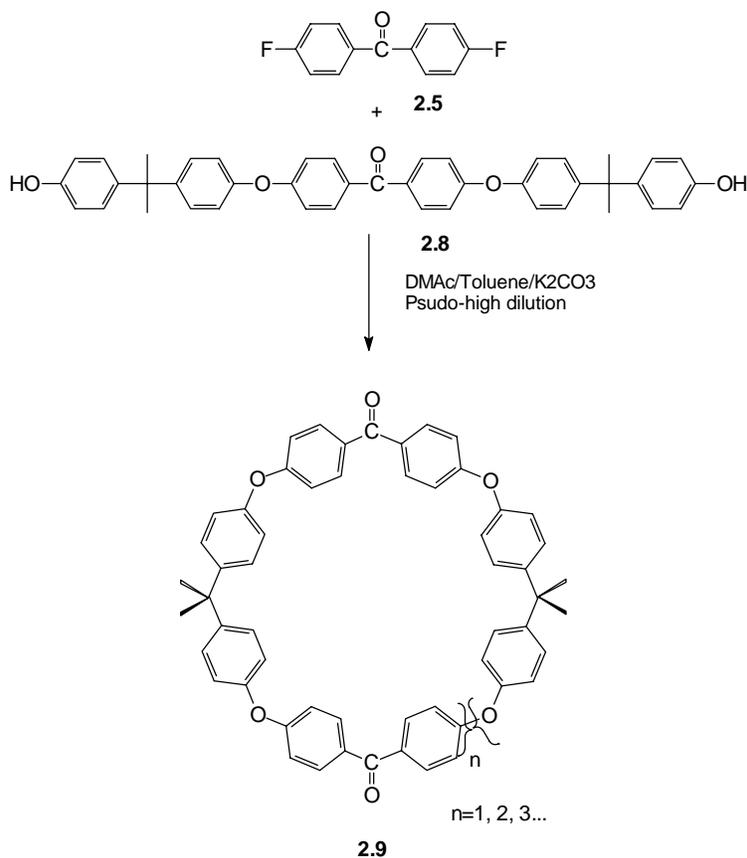


Figure 2.6. 400 MHz ^1H - ^1H COSY NMR spectrum of compound **2.8** in CDCl_3 .

2.3 Synthesis and Characterization of Cyclic Mixtures

Scheme 2.5



A cyclic mixture (**2.9**) of oligo-(oxy-p-phenylene-isopropylideneoxy-p-phenyleneoxy-p-phenylenecarbonyl-p-phenylene) was synthesized from 4,4'-difluorobenzophenone and the extended bisphenol **2.8** (Scheme 2.5). In a typical procedure, a 30 mL concentrated solution of the bisphenol and 4,4'-difluorobenzophenone (0.26 M) was injected at a rate of 1 mL/h by a syringe pump into a refluxing DMAc and toluene reservoir containing potassium carbonate. Pseudo-high dilution is necessary for the selective formation of the cyclics. Instead of using a large amount of solvent, a pseudo-high dilution condition was maintained by slow addition of the reactants into the reaction

vessel and steady low concentration of unreacted end groups was thus maintained. After the addition of the reactants, the reaction was extended for one or two days depending on the reaction temperature. The cyclic mixture was obtained by precipitating the crude product in methanol from chloroform solution.

Previously, Hay's group reported that dipolar aprotic solvents such as DMAc, DMSO and NMP are not suitable for aromatic nucleophilic substitution cyclization reactions.⁶ They found an aldol condensation side reaction of the ketone groups when DMAc was used. This side reaction was detected through NMR and MALDI-TOF-MS analysis of the final product. Their observation is in contradiction with the fact that many high molecular weight poly(ether ketone)s can be obtained based upon the same reaction in DMAc. Mullins' group has pointed out the possibility of a hydrolytic side reaction.¹⁴ DMAc can be hydrolyzed by water under basic conditions to form acetate and dimethylamine, which may participate in other side reactions. They suggested drying the solvent with molecular sieves and purging the reaction system with nitrogen to remove dimethylamine prior to adding the monomers. However, in our case no aldol condensation side reaction was detected. In our procedures, first the DMAc was azeotropically refluxed with toluene to remove water for about three to four hours

[6] Chan, K. P.; Wang Y. F.; Hay, A. S.; X. L. Hronowski; Cotter, R. J. *Macromolecules* **1995**, 28, 6705

[15] Mullins, M. J.; Galvan, R.; Bishop, M. T.; Woo, E. P.; Gorman, D. B.; Chamberlin, T. A. *Polym. Prepr. Am. Chem. Soc., Div. Polym. Chem.* **1992**, 33(2), 414.

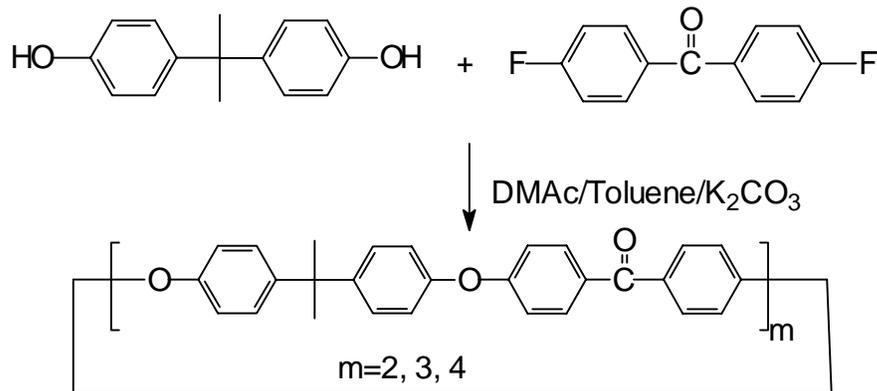
The cyclization was run several times under various conditions (Table 2.2). From Table 2.2, it can be seen that the higher the temperature the better the yield for the cyclic dimer. Mullins et al. have pointed out ¹⁵ that there is an optimum temperature for their cyclic poly(ether sulfone) system (130-140 °C). If the cyclization temperature is high, the reaction is fast, which favors the steady dilution condition, thus higher yields. On the other hand, at high temperature the phenolate can attack the cyclics to cause ring-opening and thus lower the cyclic yield. In our case, the ether linkage is less activated by the weaker electron withdrawing carbonyl group. The rate of ether exchange is slow. Therefore, the higher the temperature, the better the yield of cyclic dimer.

Table 2.2 Yield of cyclic dimer in the crude product as estimated by ¹H NMR assuming complete reaction.

Trial number	Addition Rate	Reaction Temperature (°C)	Reaction Time (h)	Wt. % of Dimer (2.9, n=1)
1	1.0 mL/h	137	96	52
2	0.8 mL/h	141	96	55
3	1.0 mL/h	164	90	65

[15] Mullins, M. J.; Galvan, R.; Bishop, M. T.; Woo, E. P.; Gorman, D. B.; Chamberlin, T. A. *Polym. Prepr. Am. Chem. Soc., Div. Polym. Chem.* **1992**, 33(2), 414.

Scheme 2.7



Bisphenol-A was reacted with 4,4'-difluorobenzophenone directly under similar pseudo-high dilution reaction conditions (Scheme 2.7). The yield of the cyclic dimer in the mixture was only about 31-36 % (weight).

Figure 2.7 compares ¹H NMR spectra of the two different cyclic mixtures obtained by reaction schemes 2.5 and 2.7. The former is referred to as the four-step method and the later as the one-step method. First, there are no signals at 6.5 and 2.5-3.0 ppm expected from the aldol condensation reaction, indicating no side reaction reported by Hay's group. Secondly, the proton adjacent to the carbonyl group of the dimer (compound **2.9**, n=1) shows a distinctive signal. So the amount of dimer can be easily calculated by proton NMR. The third characteristic is the small amount of terminal groups. No obvious terminal groups can be seen in the spectrum if the number of data acquisitions is less than 32. In order to estimate the amount of terminal groups, each spectrum had more than 500 acquisitions to ensure good signal to noise ratio.

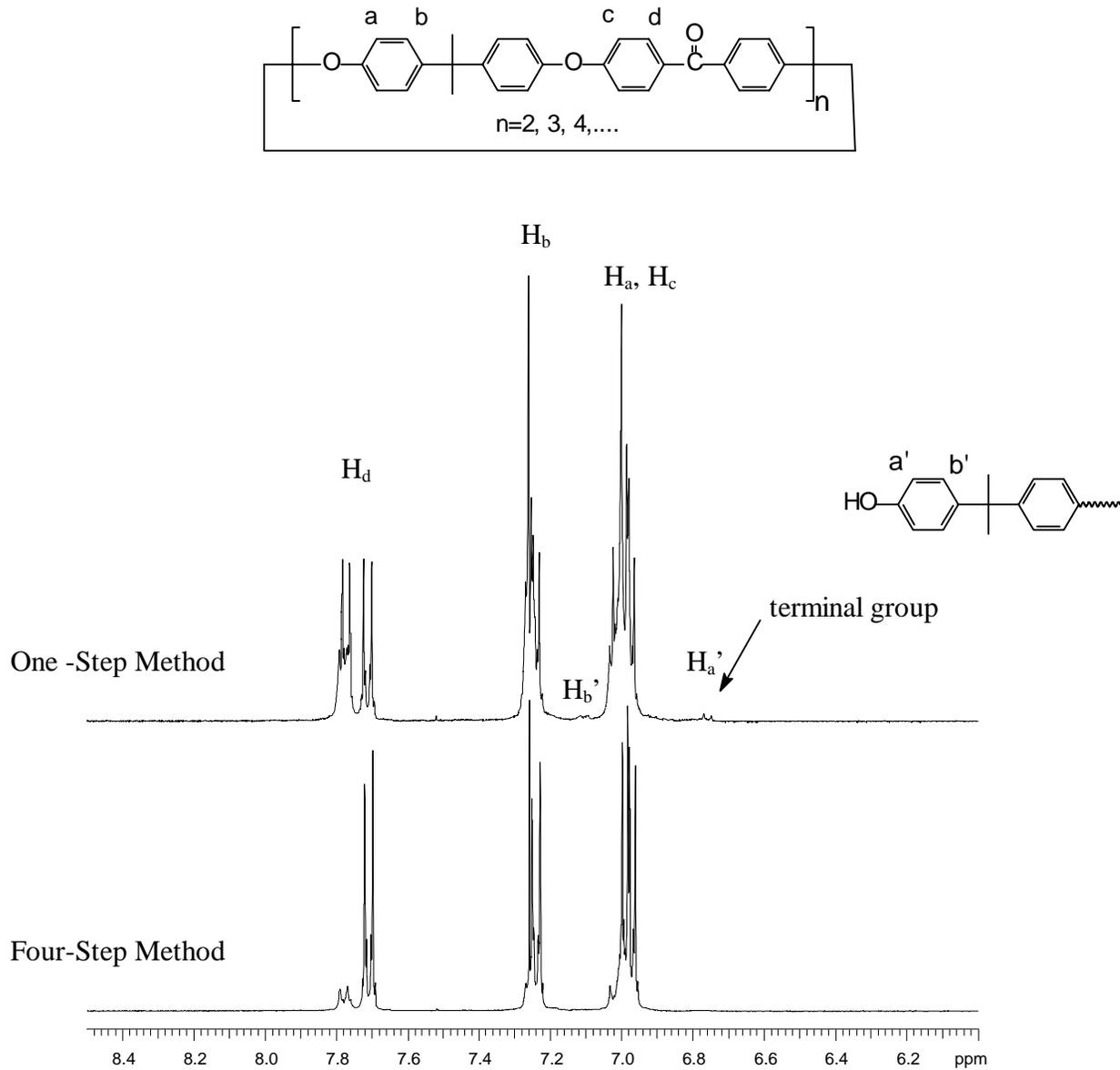


Figure 2.7 400 MHz ^1H NMR spectra in CDCl_3 of cyclic mixtures synthesized by two different methods.

Ideally, there should be only two types of terminal groups, i. e., the fluoroketone group and the phenol group. No fluoroketone signal can be seen in the spectra. The signals for OH terminated groups are located around $\delta=6.77$ and 7.12 ppm. The OH terminal group is estimated to constitute 0.94 units for the mixture from the one-step method and 0.41 units for the mixture from the four-step method per 100 repeating units. Basically the mixtures are close to pure cyclics according to terminal group analysis and the low molecular weight nature of the mixtures. The mixture from the four-step method is purer. The average molecular weights of the cyclic mixtures based upon polystyrene standards are listed below.

one-step method : $M_n=1469$ $M_w=4250$ $PID=2.9$

four-step method : $M_n=977$ $M_w=3147$ $PID=3.2$

The average molecular weight of the mixture from the one-step method is higher than that from the four-step method, though the distribution is slightly narrower. The difference is because of the cyclic distribution. The average molecular weight of each mixture corresponds to 3 to 4 repeating units.

The formation of almost pure cyclics is also seen by the matrix assisted laser desorption ionization time-of-flight mass spectrum (MALDI-TOF-MS) of the mixtures (Figure 2.8). For the one step synthesis molecular ions of cyclics are observed up to 10 repeating units. There are no signals of any linear oligomers or aldol condensation side products. Table 2.3 lists the calculated molecular ion

peaks vs. the experimentally determined values. There is a complete match of the two within the experimental error.

Table 2.3 Positive ion MALDI-TOF-TOF-MS (in dithranol matrix) of cyclic mixture **2.0** synthesized according to Scheme 2.7.

signal (m/z)	assignment	calculated m/z	deviation*
798	$[M_2-CH_3+H]^+$	798	0
813	$[M_2+H]^+$	813	0
1220	$[M_3+H]^+$	1219	-1
1627	$[M_4+H]^+$	1626	-1
2033	$[M_5+H]^+$	2032	-1
2440	$[M_6+H]^+$	2438	-2
2847	$[M_7+H]^+$	2844	-3
3255	$[M_8+H]^+$	3250	-5
3657	$[M_9+H]^+$	3656	-1
4070	$[M_{10}+H]^+$	4063	-7

* deviation=experimental value-calculated value

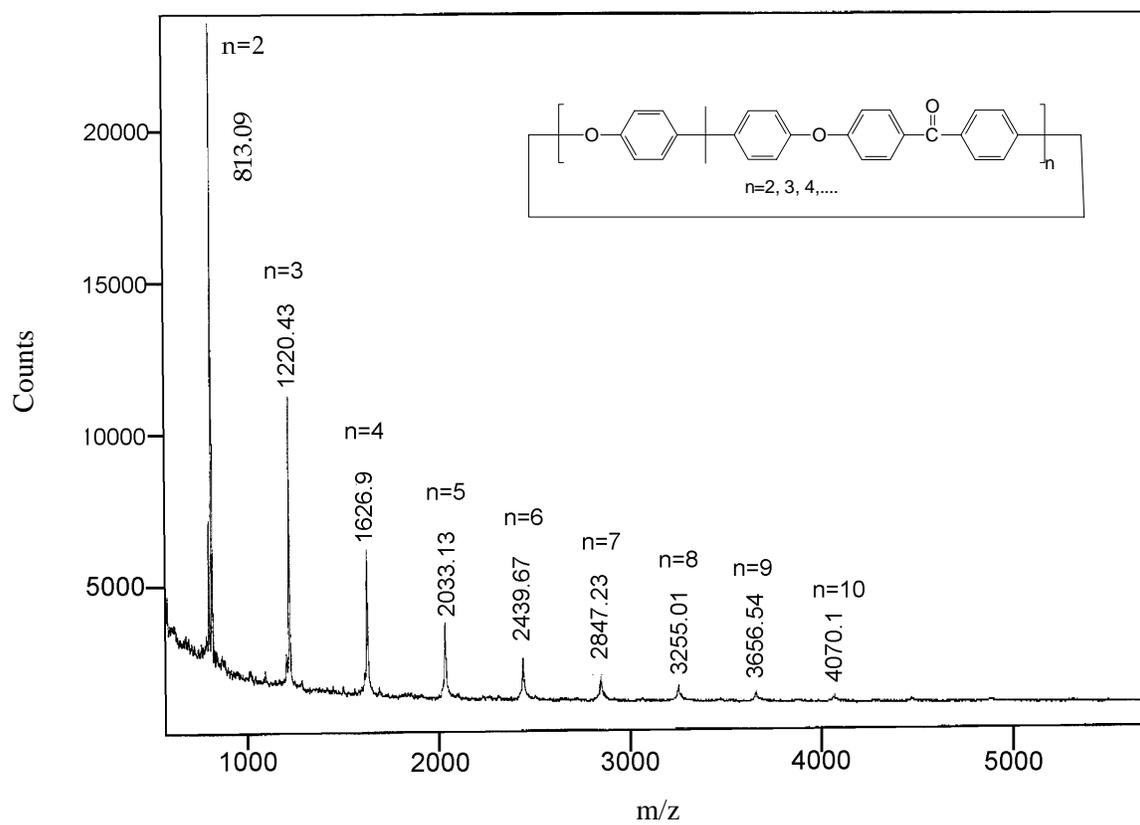


Figure 2.8 MALDI-TOF-mass spectrum of cyclic mixture **2.9** synthesized according to Scheme 2.7.

The composition of the cyclic mixtures synthesized by the one-step and four-step methods can also be analyzed by Reverse Phase HPLC (RP-HPLC) and GPC. Because macrocyclic ether ketone compounds are polar compounds, they are most suitably analyzed by RP-HPLC. C₈ columns generally have better efficiency or better resolution, while C₁₈ columns allow higher loading of samples. Since our samples have many components, to get better sensitivity for each component more sample is needed. Therefore a C₁₈ column was used. The most common solvent combinations for RP-HPLC analysis are methanol-water, acetonitrile-water and THF-water. The organic solvents are used to reduce the polarity of water. THF is a good solvent for the cyclic mixtures and it was used as the organic solvent. The best composition of the mixed solvent depends on the molecular weight as well as the nature of compounds to be analyzed. It was found that the combination of 65:35 (v/v) THF/water gave the best results. If too much THF is used, the elution is too fast, giving poor resolution. If too little THF is used, the analyte will not come out or only the first few peaks are observed. However, a constant solvent will not be good for analyzing all the components in the cyclic mixture. The higher oligomers will not come out under a constant solvent strength. Therefore, a linear solvent gradient was used. The amount of the THF was gradually increased in line with the late elution of the higher oligomers. Figure 2.9 shows the RP-HPLC chromatograms of the cyclic mixtures obtained by one-step and four step methods. For the four-step method, the highest peak eluted at 3.4 minutes (63 %) is due to the dimer (n=2). The two smaller peak at about 5.9 and

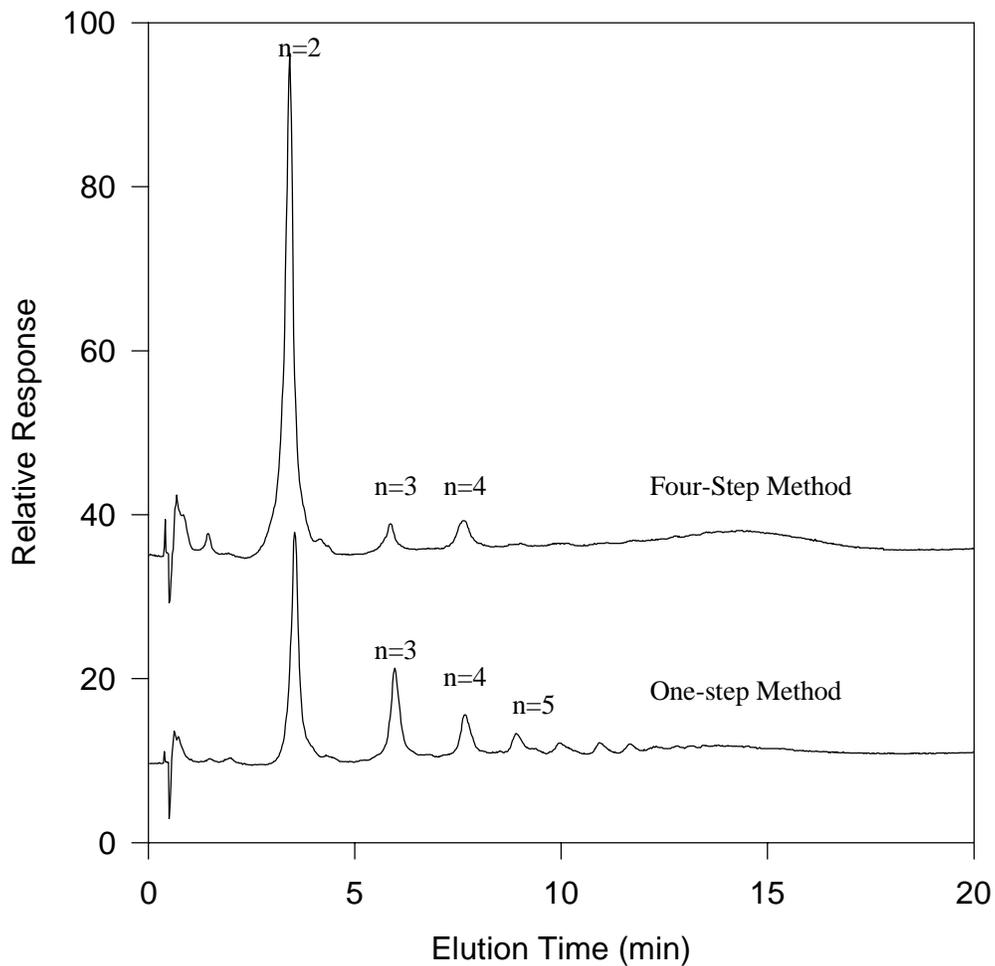
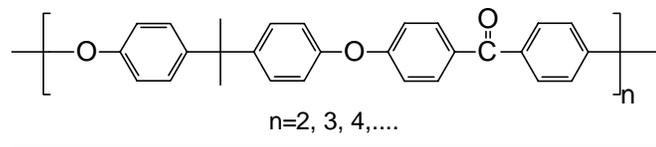


Figure 2.9 HPLC chromatograms of cyclic mixtures synthesized by two different methods.

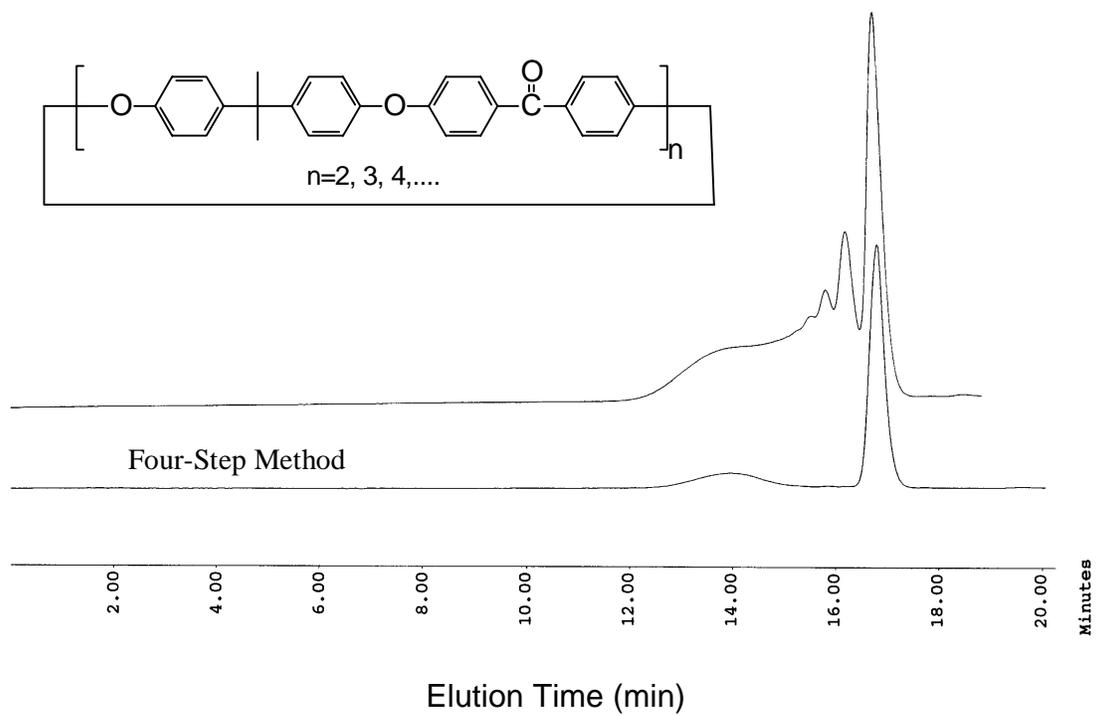


Figure 2.10. GPC chromatograms of cyclic mixtures synthesized by two different methods.

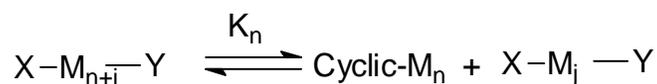
7.6 minutes are due to the trimer (n=3) and the tetramer (n=4). No obvious peaks of higher oligomers can be seen on the chromatogram. On the RP-HPLC chromatogram of the cyclic mixture from the one-step method, oligomers with repeating units up to 7 are obvious. The composition of the cyclics are listed in Table 2. 4.

Table 2.4 Distribution of the cyclics (wt %) in the cyclic mixtures----comparison of one- step and four-step method.

Number of Repeating units	2	3	4	5
One Step Method (HPLC)	44	17	8	7
Four Step Method (HPLC)	63	3	4	
One Step Method (GPC)	36	16	10	6
Four Step Method (GPC)	77			
One Step Method (¹ H NMR)	37			
Four Step Method (¹ H NMR)	79			

The cyclic distribution can be analyzed by GPC as well (Figure 2.10). GPC is probably more accurate than HPLC not because of its better resolution, but because of the more accurate integration of the whole area on the chromatogram. The amount of dimer in the mixture detected by GPC agrees better with measurements by proton NMR.

The classical theory of cyclic distribution in a ring-chain equilibrium system was developed by Jacobson and Stockmayer.¹⁶ They assumed that there is complete ring-chain equilibrium as shown below.



Based upon this equilibrium, then $K_n = [\text{Cyclic-}M_n] / p^n$

Where p is the extent of reaction

n is the number of repeating units

K is the equilibrium constant

M is the repeating unit

X, Y are reactive end groups

In the case that the extent of reaction p equals to 1, $K_n = [\text{Cyclic-}M_n]$

The equilibrium constant K_n can be calculated according to the probability of the reactive ends meeting each other assuming the probability density is a Gaussian function. The following equation is obtained.

$$K_n = [\text{Cyclic-}M_n] = C n^{-\gamma} \quad \gamma = 2.5$$

There are a number of systems such as cyclic polysiloxanes that were found to obey the J-S theory qualitatively. Hay et al, recently applied the theory to their cyclic ether ketone system⁶. They found a γ value of 2.4, which is very close to the theoretical value.

[16] Jacobson, H.; Stockmayer, W. H. *J. Chem. Phys.* **1950**, 18, 1600.

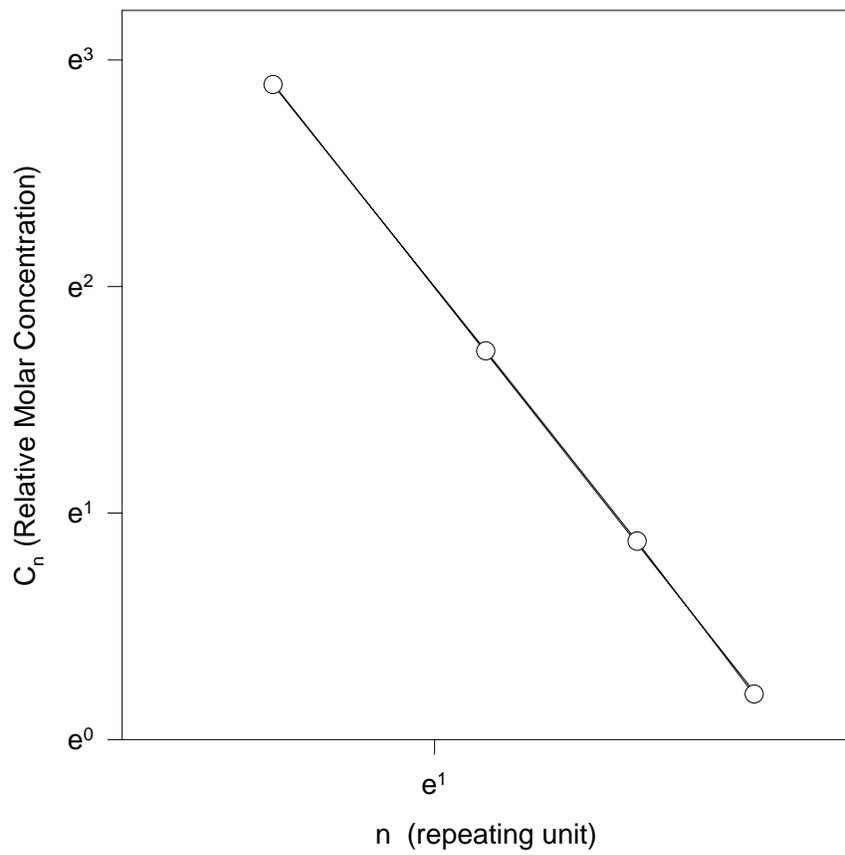


Figure 2.11. Log-Log plot of C_n vs n .

Using the data in table 2.3 for the cyclic distribution of the mixture from the one-step method, a similar linear plot (Figure 2.11) of $\ln(n)$ vs $\ln(C_n)$ (C_n is the relative molar concentration of cyclic n-mer) gives a γ value of 2.9. This is apparently close to the distribution predicted according to J-S theory. It should be pointed out that for the mixture obtained from the four-step method, a similar linear plot can not be made. This clearly suggests that the cyclic distribution is not thermodynamically controlled. If it is thermodynamically controlled, the final composition should be independent of the starting materials. In other words, the system does not meet the critical equilibrium condition of J-S theory, although the distribution from the one-step mixture apparently can be described by the J-S equation. The reason is that the system is far from ring-chain equilibrium. This can be seen from another point of view. According to the reaction scheme 2.5, the number of repeating units should be even numbered. However, there is about 3 % of cyclic trimer in the mixture according to HPLC. The formation of the odd numbered cyclics is due to the backbiting ether exchange reaction. Since the amount of trimer is very small, the backbiting ether exchange reaction is slow and the reaction is far from ring-chain equilibrium.

DSC thermograms of the two different cyclic mixtures are shown in Figure 2.12. The mixture from the one-step method shows a broad melting peak at around 355 °C, while the mixture from four-step method gives a melting peak at 378 °C, which is closer to the melting point of the pure cyclic dimer (386 °C).

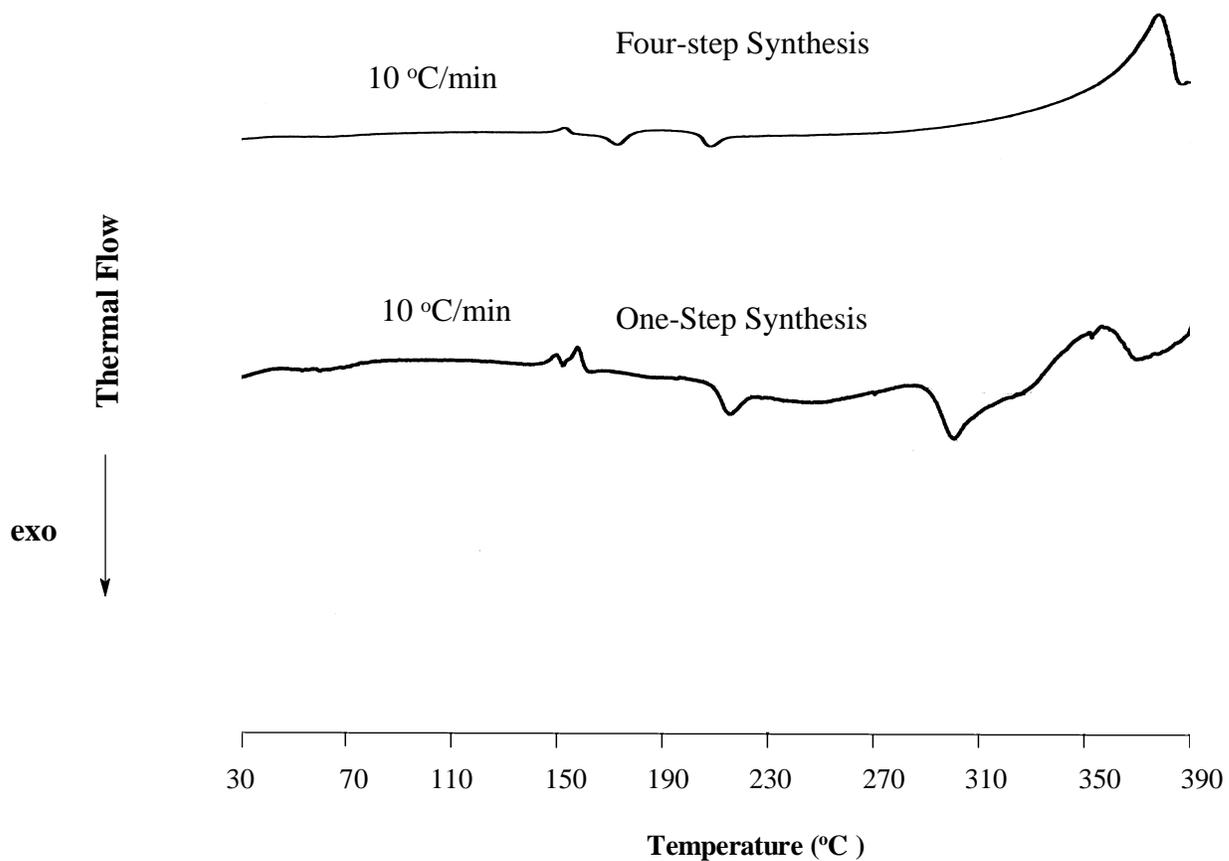


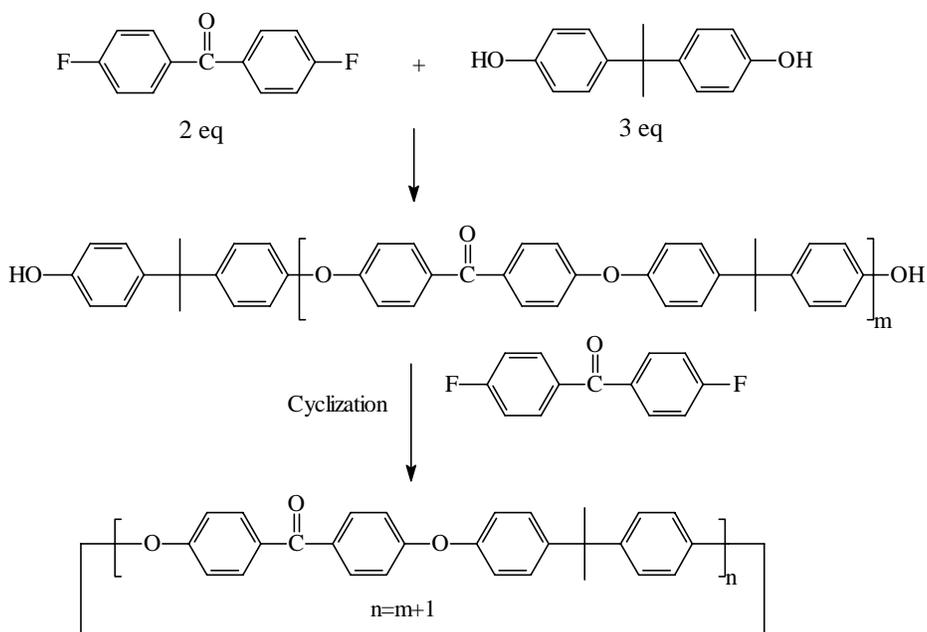
Figure 2.12. DSC thermograms of cyclic mixtures synthesized by two different methods.

The difference in the thermal behaviors can also be explained by the difference in the cyclic distribution, i. e., the amount of cyclic dimer in the mixtures. This result clearly suggests that the melting point is mainly determined by the amount of dimer present in the mixture.

2.4 Synthesis of Macroscopic Mixture by the Linear Oligomer Approach.

The fact that the cyclic distribution is kinetically controlled and the melting point of the cyclic mixture is mainly determined by the amount of the highest melting point cyclic dimer prompted us to devise a method to reduce the amount of the cyclic dimer in the mixture. This approach is outlined in Scheme 2.8.

Scheme 2.8



In this approach, first, linear oligomers were synthesized with an average length of two repeating units. The average molecular weight of the oligomers is

controlled by the stoichiometric ratio of the bisphenol-A and 4,4'-difluorobenzophenone. Since the size is mainly determined by the combined length of the starting materials, the amount of dimer should be reduced. In our initial trial, 3 equivalents of 4,4'-difluorobenzophenone and 2 equivalents of bisphenol were used. The fluoroketone terminated oligomers were isolated first and then mixed with one equivalent of bisphenol-A. This mixture was cyclized to form a cyclic mixture. According to NMR the amount of cyclic dimer was 11 %. However, there was a significant amount of phenol terminal group (3 %). This is because of the difficulty to quantitatively isolate the linear oligomers and the possibility of reaction of the fluoroketone with some impurity. In our second trial, the bisphenol-A was used in excess and the linear oligomer was not isolated, but was directly mixed with a stoichiometric amount of 4,4'-difluorobenzophenone. The slurry solution was added in three portions over 36 hours to a large amount of solvent. According to the NMR spectrum, there is only 21 % of the dimer. The NMR spectrum shows no obvious signal for terminal groups. According to the GPC chromatogram the cyclic mixture made by this method consists of 17 % dimer, 10 % trimer, 8 % tetramer and 5 % pentamer with the rest being high oligomers. The macrocyclic mixture is amorphous and has a glass transition at 146 °C on the second heating.

2.5 Characterization of Pure Dimer and Tetramer

The isolation of the pure cyclic dimer was straightforward, the cyclic dimer is less soluble in chloroform than the higher cyclics. By washing out the other

products from the crude product with chloroform or toluene as much as 59 % of dimer can be isolated. The other oligomers are quite soluble in chloroform or toluene. The cyclic trimer and tetramer can be obtained by column chromatography using silica gel and ethyl acetate/hexanes (v/v=1:2).

Figures 2.13 and 2.14 show the ^1H and ^{13}C NMR spectra of the cyclic dimer, respectively. The proton NMR spectrum has four doublets and the methyl singlet is located at $\delta=1.71$. There is no terminal group in the spectrum, establishing its cyclic structure. The ^{13}C NMR spectrum has eleven peaks as required and again no terminal group signal. The IR spectrum (Figure 2.15) of the dimer has the ketone and ether linkage absorptions. The OH group has disappeared. The carbonyl band shifts to higher wavenumber (1656 vs 1636 cm^{-1}) compared to the linear precursor **2.8**. This is due to the ring strain in the dimer. A similar phenomenon was observed for cyclic carbonate.¹⁷

The size of the macrocycle was determined by the FABMS spectrum as shown in Figure 2.16. The pseudo-molecular ion peak ($[\text{M}+\text{H}]^+$) at $m/z=813.3$ exactly matches the calculated value (813.31). DSC thermograms of the macrocycle at a heating rate of $10\text{ }^\circ\text{C}/\text{min}$ are shown in Figure 2.17. On the first heating there is an exothermic peak at $161\text{ }^\circ\text{C}$, which is probably due to crystallization of the macrocycle. There is a sharp melting peak at $383\text{ }^\circ\text{C}$. The melting enthalpy is $\Delta H=81\text{ J/g}$. The sample was heated to $410\text{ }^\circ\text{C}$ followed by gradually cooling to room temperature. On the cooling curve, there is a T_g at

[17] Brunelle, D. J.; Garbaskas, M. F. *Macromolecules* **1993**, 11, 2725.

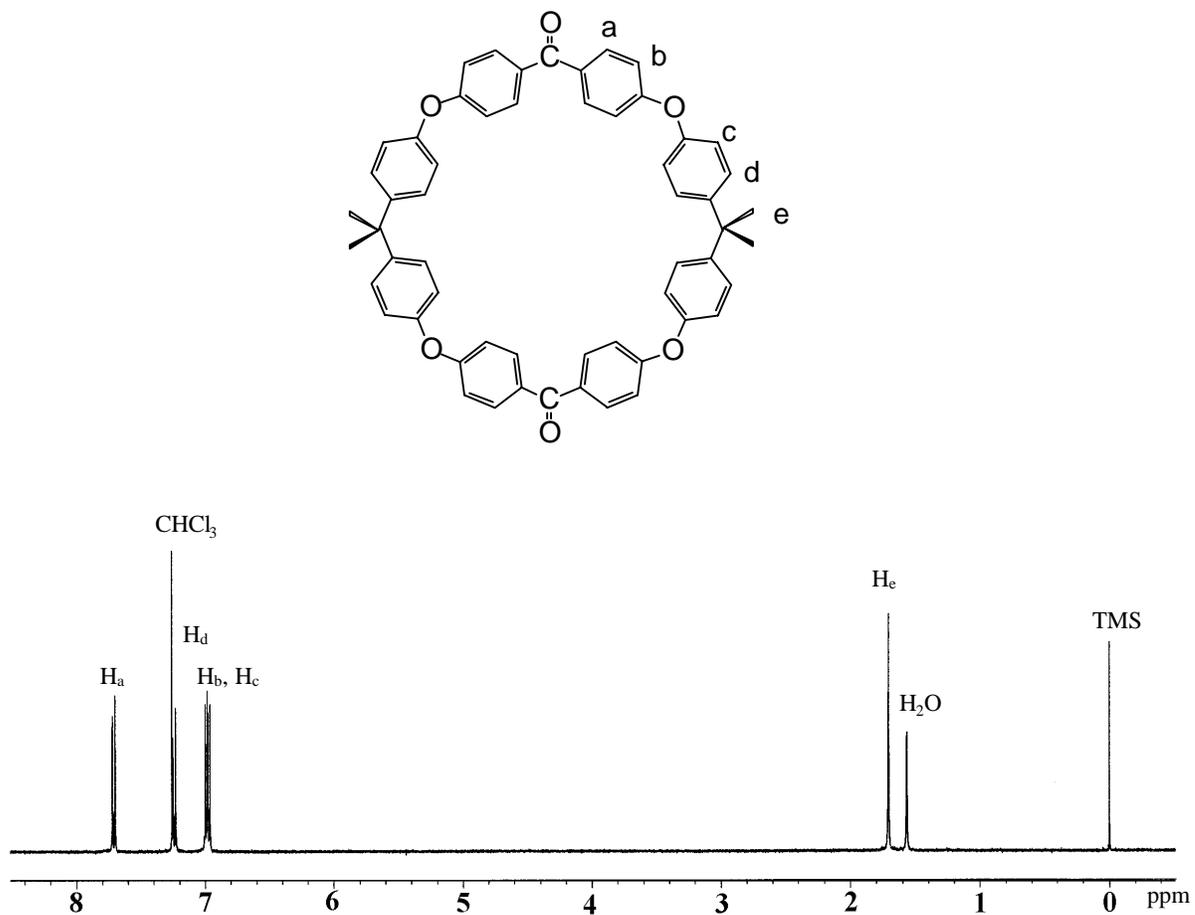


Figure 2.13. 400 MHz ¹H NMR spectrum of macrocyclic dimer (**2.9**, n=2) in CDCl₃.

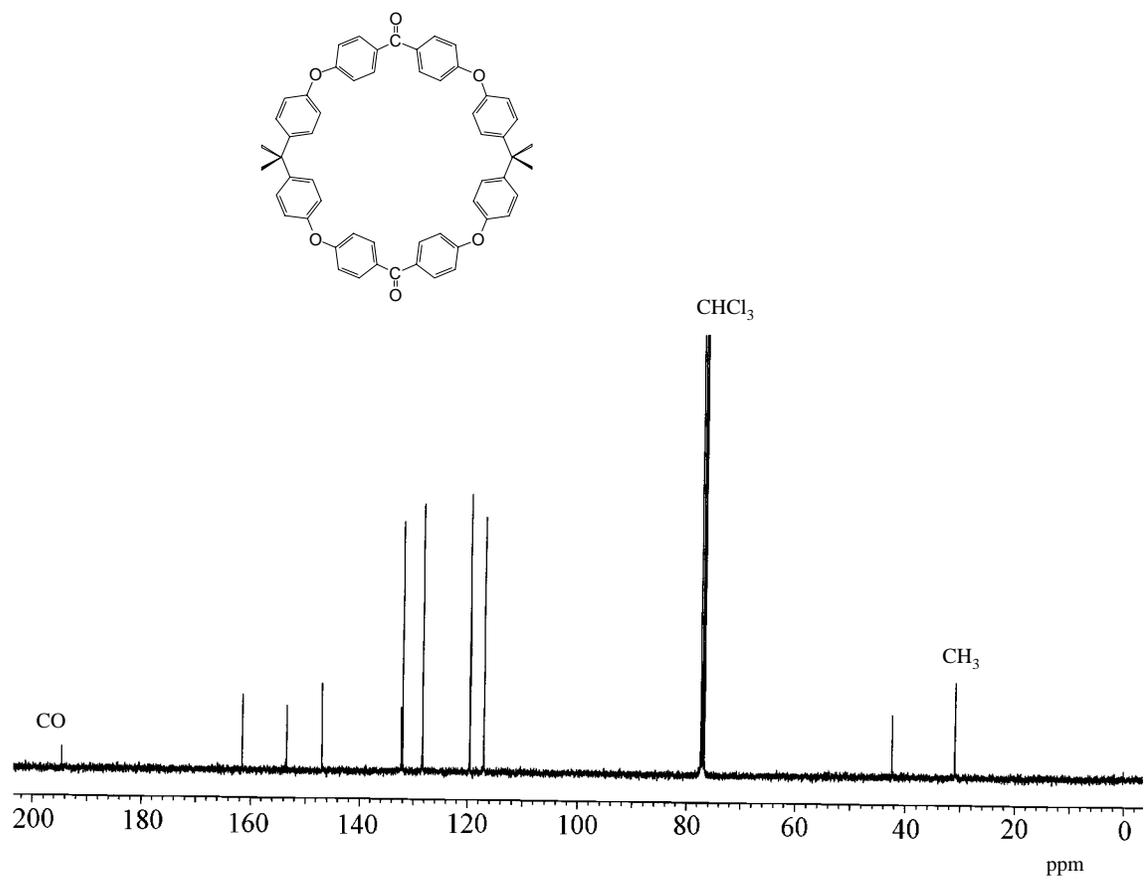


Figure 2.14. 100 MHz ¹³C NMR spectrum of cyclic dimer (**2.9**, n=1) in CDCl₃.

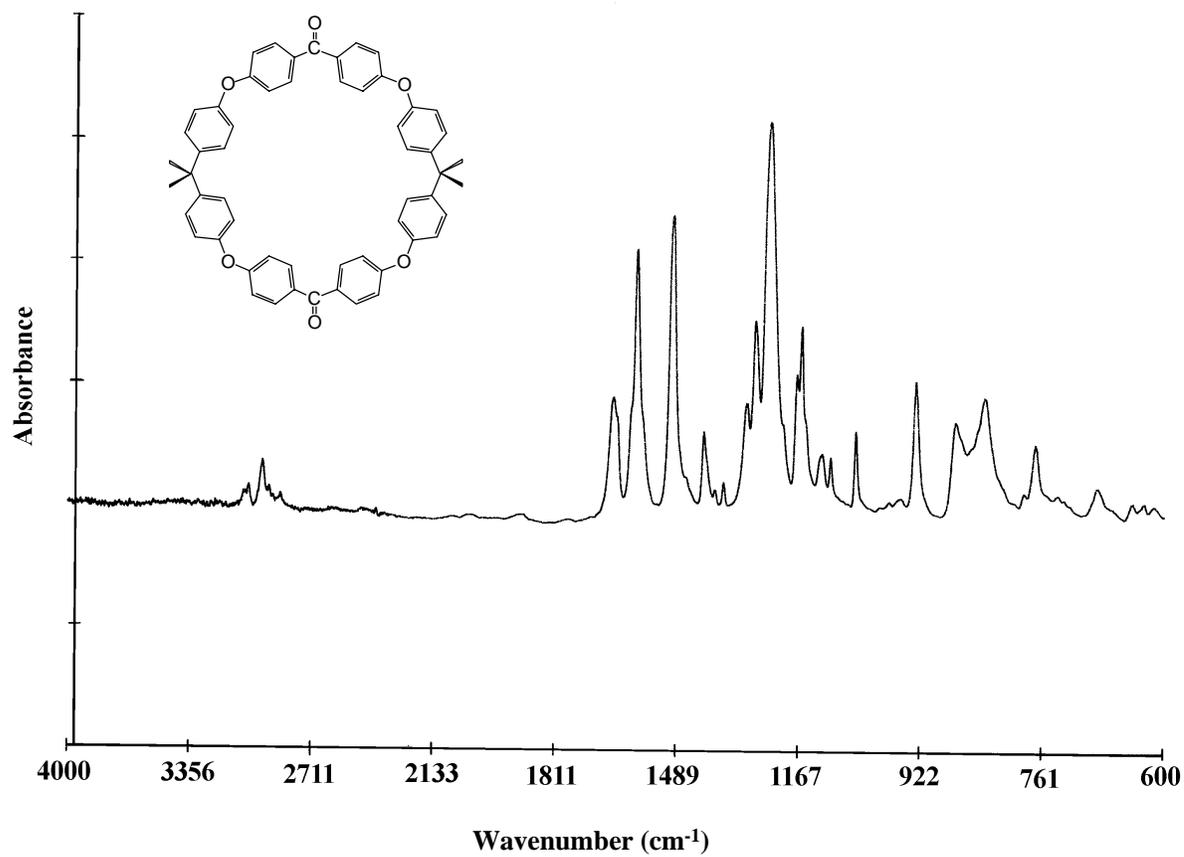


Figure 2.15. IR spectrum of cyclic dimer (**2.9**, n=1) (KBr pellet).

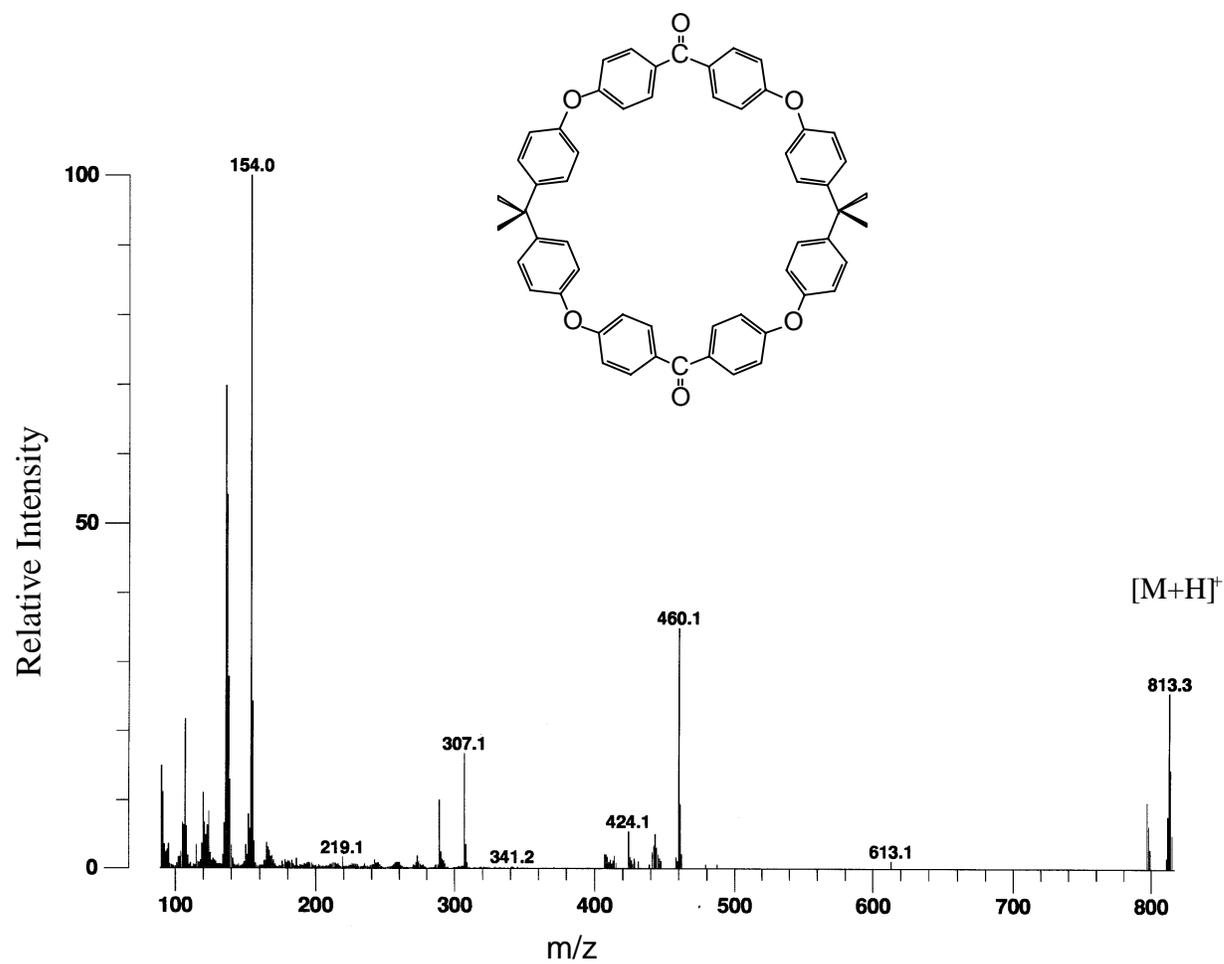


Figure 2.16. FABMS (in 3-NBA matrix) spectrum of cyclic dimer (**2.9**, $n=1$).

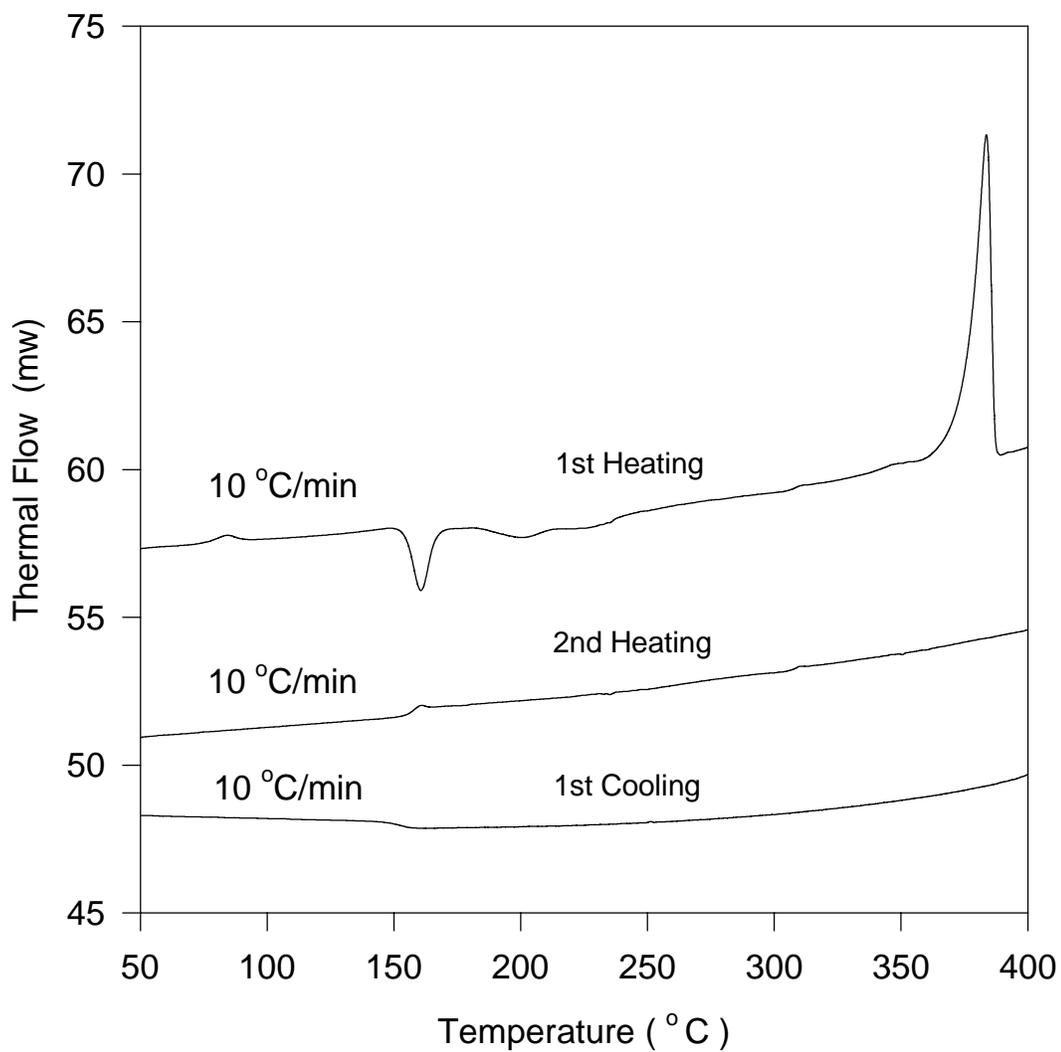


Figure 2.17. DSC thermograms of cyclic dimer in nitrogen.

155 °C. On the second heating there is only a glass transition at 157 °C, corresponding to the glass transition seen on the cooling curve. Examining the final sample indicated that a tough polymer was obtained and it was insoluble in chloroform, suggesting the polymer was crosslinked. Spontaneous polymerization upon melting is probably due to some residual potassium salt in the sample. Hay's group has noticed that K_2CO_3 is quite effective for initiating the ring-opening polymerization of the cyclic poly(ether ketone)s.¹⁸ The literature reported glass transition temperature of the corresponding high molecular weight linear polymer is 155 °C, indicating the polymerized sample from DSC was only slightly crosslinked.

The thermal stability of the macrocycle is indicated by the TGA experiment. The 5 % weight loss temperature of the macrocycle is 463 °C in air and 476 °C in nitrogen atmosphere. There is about 40 % char yield in the nitrogen and only a few percent of char yield in the air.

The carbonyl groups in the cyclic dimer can be easily reduced to hydroxyl groups with $NaBH_4$ in THF. The complete reduction was confirmed by 1H NMR.

The cyclic tetramer was isolated by column chromatogram. Its NMR spectrum (Figure 2.19, 2.20) is too similar that of the dimer. The size of this tetramer was confirmed by the molecular ion peak in the FABMS ($[M+H]^+$ 1727.3).

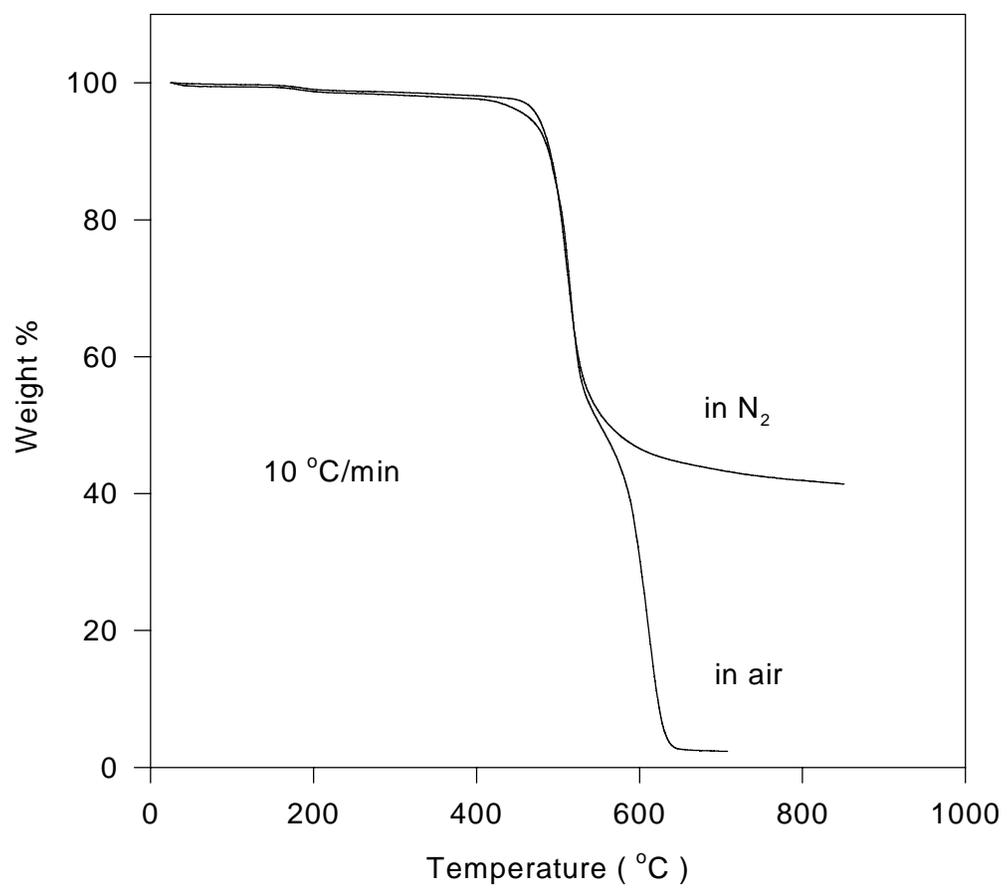


Figure 2.18. TGA thermogram of cyclic dimer (2.9, n=1).

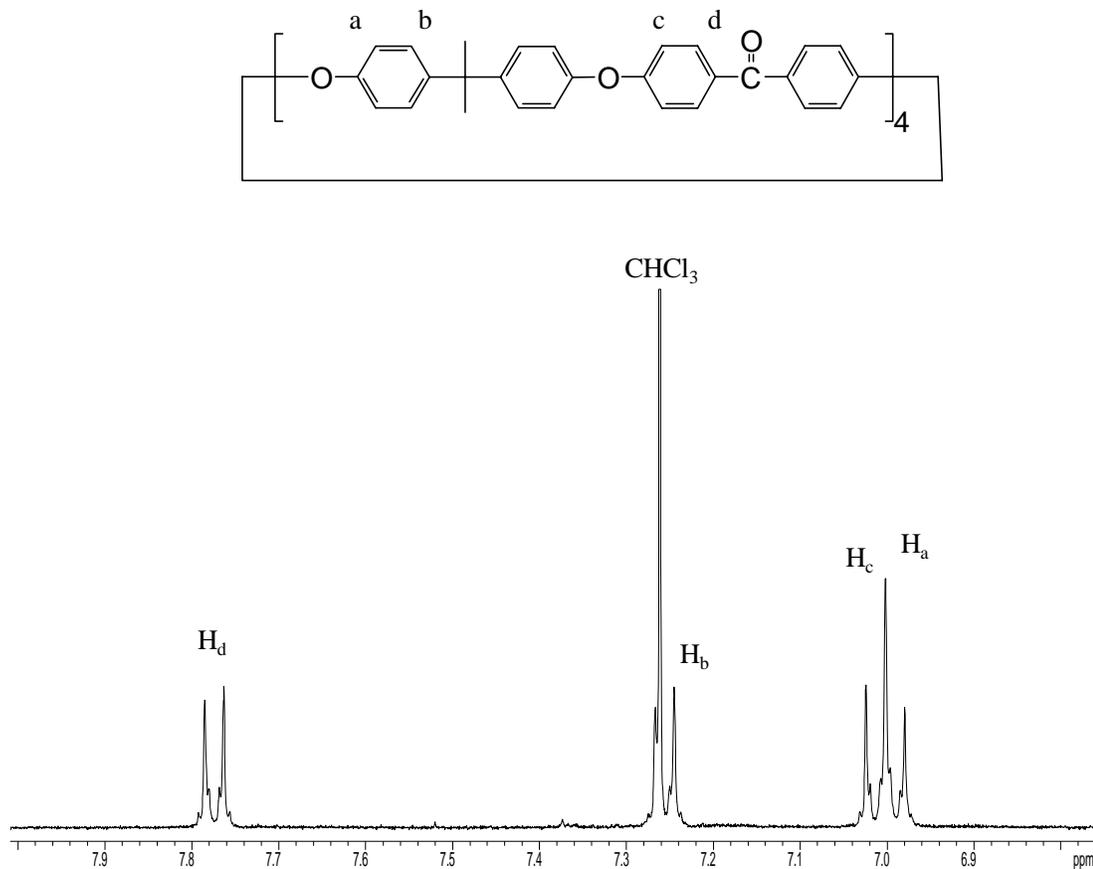


Figure 2.19. 400 MHz ^1H NMR spectrum of macrocyclic tetramer (**2.9**, $n=3$).

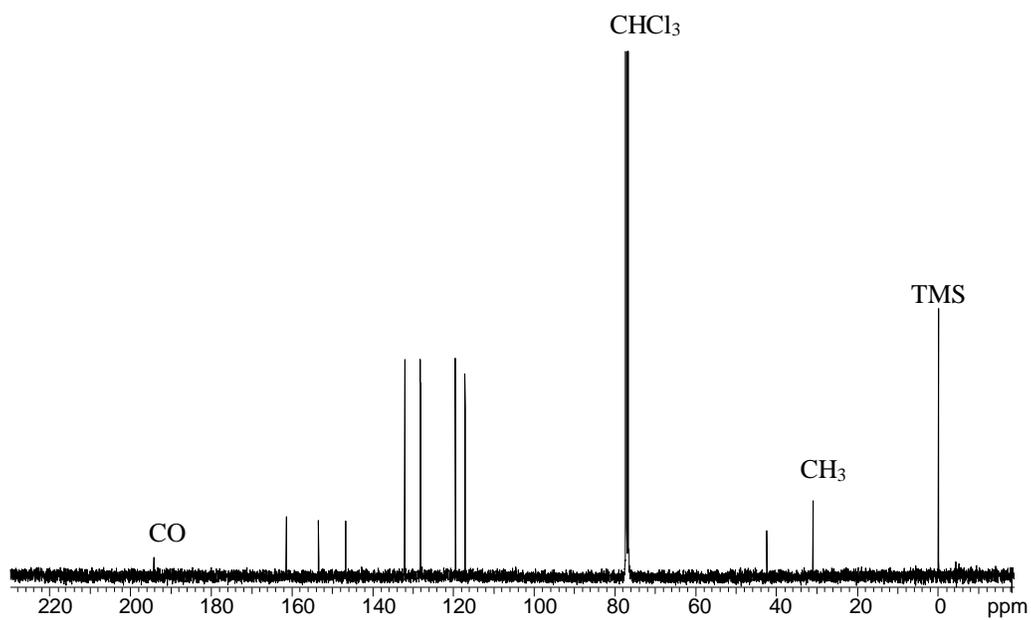
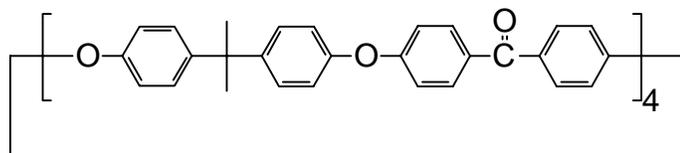


Figure 2.20. 100 MHz ^{13}C NMR spectrum of cyclic tetramer (**2.9**, $n=3$).

2.6 X-ray Structure of Macrocyclic Dimer

The X-ray structure of macrocyclic monomers has been the subject of numerous studies.^{9,18,19} The structural information is useful to get geometric parameters as well as the conformational features of macrocycles. Single crystals of the 40-membered macrocyclic dimer **2.9 (n=1)** were obtained by slow evaporation of a chloroform solution. After refinement the R value is 0.1424, which is high. The high R value is due to the disordered chloroform molecules in the crystal structure. Nevertheless, the bond lengths such as C(Ph)-O, C(Ph)-CO, C=C, C=O are very close to the values of a related macrocycle reported from our group.¹⁸ The conformational features are evident from the crude structure (Figure 2.21). The macrocycle adopts an open flat conformation with approximately a rectangular shape, similar to the 40-membered diether disulfone macrocycle reported by Colquhoun and Williams.⁹ The transannular centroid-to-centroid distance between rings C(9)-C(10) and C(9A)-C(10A) is 13.08 Å. The corresponding distance between the centroids of ring C(24)-C(25) and C(24A)-C(25A) is 10.17 Å. The cavity size is more than sufficient for other molecules to thread. These two dimensions are slightly less than reported for the diether disulfone macrocycle (14.98 X 12.30 Å),⁹ which indicates that substituting the

[18] Chen, M.; F. Fronczek; Gibson, W. *Macromol. Chem. Phys. Macromol.*

Chem. Phys., **1996**, 197, 4069.

[19] Ovchinnikov, Y. E.; Nedelokin, V. I.; Ovsyanikova, S. I.; Struchkov, Y. T. *Izv.*

Akad, Nauk, Ser. Khim. **1995**, 1460.

sulfone groups with ketone moieties increases the flexibility of the macrocycle. The diether diketone macrocycle tends to have a more collapsed conformation relative to the disulfone. The size difference is further proved by GPC experiments. In the GPC chromatogram, the disulfone is eluted ahead of the diketone. The more rigid conformation of the disulfone macrocycle is also evident from the melting point difference of the two macrocycles. The disulfone macrocycle has a melting point of 505 °C compared to 386 °C for the diketone macrocycle.

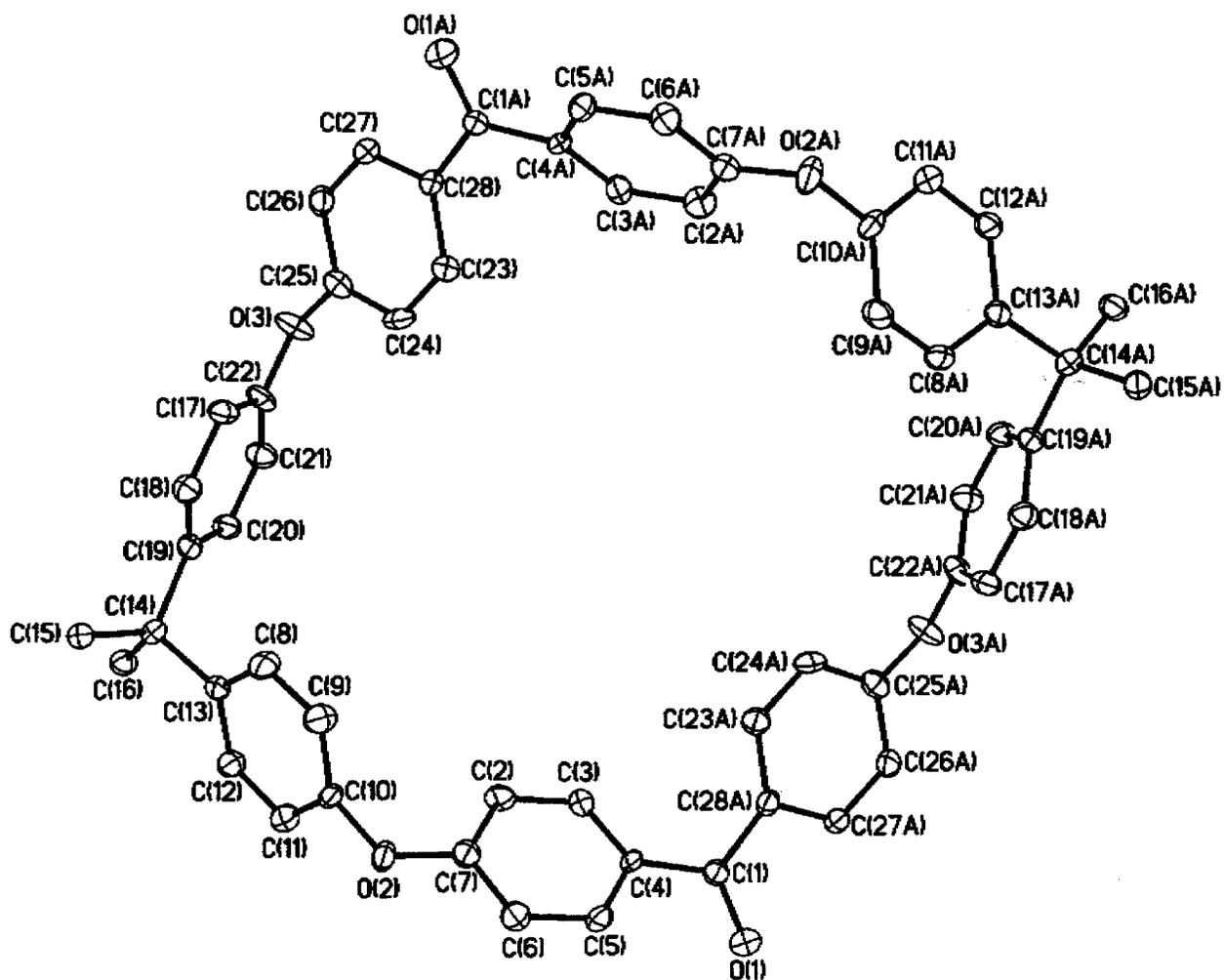


Figure 2.21. Single crystal X-ray structure of cyclic dimer (2.9, n=1).

2. 7 Conclusions

1. DMAc is an appropriate solvent to synthesize macrocyclic oligo(arylene ether) ketone monomers by nucleophilic aromatic substitution reactions under carefully controlled reaction conditions. This is supported by NMR and MALDI-TOF-MS analyses.
2. Sharply different ring size distributions of the cyclic mixtures from two different syntheses suggest that formation of the cyclics is mainly controlled by the kinetics of the reaction (linear growth vs cyclization). The amount of backbiting reaction is very small and thus the ring-chain equilibrium is not reached in this system. Based on this understanding, a novel linear oligomer approach was devised, which effectively reduced the proportion of high melting point dimer.
3. The X-ray structure of the cyclic dimer was determined and the macrocycle has a large enough cavity to be threaded by other molecules. The X-ray structure suggests that sulfone group makes a macrocycle more rigid than the ketone group. This is further supported by GPC experiments.

2.8 Experimental

Materials. Bisphenol-A was purified by recrystallization in toluene three times. Benzyl bromide, N,N-dimethylacetamide, potassium carbonate, toluene, chloroform, 4,4'-difluorobenzophenone, trimethylsilyl chloride, sodium thiosulfate, acetonitrile, sodium iodide, potassium bromide were used as supplied by either Fisher Scientific or Aldrich.

Measurements. A Sage Instruments syringe pump model 355 was used to control the addition of reactants in the cyclization reactions. Melting points were determined on a Haake-Buchler capillary melting point apparatus and were corrected. ^1H and ^{13}C NMR experiments were performed at room temperature on Bruker WP 270 MHz or Varian Unity 400 MHz NMR spectrometers using tetramethylsilane as the internal standard. Infrared spectra (KBr pellets) were recorded on a Nicolet MX-1 FTIR spectrometer. Column chromatography was performed using silica gel 60 (32-63 micron mesh). TGA and DSC thermograms were obtained from Perkin-Elmer Model TGA-7 and Unix DSC 7 or DSC 4 models under nitrogen and air at heating rates of 10 °C/min. Reverse-phase HPLC analyses were performed on an ISCO dual pump HPLC system comprising two Model 2350 pumps and UV/Vis detector set at 275 nm. Tetrahydrofuran/water linear gradients were used for elution of the analytes on a Novapak C-18 reverse-phase column at a flow rate of 1.5 mL/min. The gradient used for analysis was as follows: Solvent A. THF; solvent B, 65:35 (v/v)THF/water, the amount of B was changed from 100 % to 20 % over a period

of 20 minutes. The system was interfaced with the ISCO ChemResearch Chromatographic Data Management/System, used for data analyses. GPC analyses were done on an ISCO Model 2300 HPLC pump equipped with two Polymer Laboratories PLgel 5 μ m MIXED-D 300X7.5 mm columns arranged in series with THF as the eluent and UV detection at 254 nm. Polystyrene was used as the standard for calibration. FABMS was obtained from Washington University at St. Louis Mass Spectroscopy Center; the matrix was 3-nitrobenzyl alcohol.

Growth of Single Crystal of Dimer and X-ray Analysis.

About 10 mg of macrocycle **2.9** (n=1) sample was dissolved in 0.5 mL chloroform. The solution in a 1 mL vial capped with aluminum foil was slowly evaporated at room temperature. After 2 or 3 days, clear needle-like single crystals with size about 0.3 mm x 0.3 mm x 5 mm were obtained. The X-ray structural analysis was performed on a CCD-detector equipped Siemens P4 diffractometer with molybdenum-target tube. Of 15361 data collected, there were 5215 independent reflections. The structure was solved by SHELTXL-plus software and refined by full-matrix least-square on F^2 . Final R=0.1424.

Synthesis of Monobenzyl Ether of Bisphenol-A (MBBE).

Bisphenol-A (75 g, 0.33 mol) and potassium carbonate (45.25 g, 0.33 mol) were added to a solution of 400 mL DMAc and 200 mL toluene in a 1L three-neck round flask equipped with a Dean-Stark trap under stirring. The oil bath

temperature was maintained at reflux to remove water from the system for about 4 hours until no more water came out. Then the temperature of the oil bath was adjusted to 120 °C. A 20 % solution of benzyl bromide (10 mL, 64 mmol) in DMAc was added dropwise over 2-3 hours. The reaction was complete in about 2 hours after complete addition. After cooling down, the salts were removed by filtration and solvent was removed by a rotatory evaporator to get a sticky product. Three different methods were tried to purify the product. In method A, the crude product was neutralized with 5 % HCl to pH=7 and then exhaustively extracted with chloroform. The chloroform phase was washed with 10 % aqueous NaOH until no bisphenol-A was left (checked with HCl). Then the chloroform was removed and a yellow liquid was obtained. The yellow liquid was dissolved in methanol and poured into water to precipitate out a white solid. The solid was redissolved in methanol and the undissolved solid (DBBE) was filtered off. The clear solution was added to water to precipitate a white solid. The solid was dried and recrystallized in hexanes/1-hexanol (10:1) and pure product was obtained. In method B, the sticky crude product was dissolved in 10 % aqueous NaOH to ensure MBBE was completely transformed to its salt. The solution was washed with chloroform. Then the chloroform phase was extracted with 10 % NaOH. Chloroform was removed to get a white solid, which was acidified with 5 % HCl in methanol. The undissolved solid (DBBE) was separated and the methanol solution was added dropwise to get a white precipitate. The precipitate was dried and recrystallized in hexane/1-hexanol (v/v 10:1) to get pure MBBE. In method C, bisphenol-A was removed by washing the sticky solution with 20 %

NaOH. The remaining steps were same as those in method B. Yields are listed in table 2.1. Mp 109.7-111.1 °C (lit.¹⁰ mp 107-108 °C), ¹H NMR (400 MHz, CDCl₃): δ=7.24-7.41 (m, 5H), 7.09 (d, 2H, J=8.8 Hz), 6.88 (d, 2H, J=8.8 Hz), 6.72 (d, 2H, J=8.8 Hz), 5.03 (s, 2H), 4.01 (s, 1H). FTIR (KBr): 3216 (OH), 1609, 1510 (C=C), 1231 (C-O-C) .

Synthesis of Monobenzyl ether of Bisphenol-A by Interfacial Method.

To a 2 L round bottom flask equipped with a mechanical stirrer, nitrogen inlet and a condenser were added bisphenol-A (45.66 g, 0.200 mol), KOH (22.4 g, 0.200 mol) and 1250 mL deionized water. The mixture was heated to about boiling and benzyl bromide (34.21 g, 23.8 mL, 0.2 mol) was added from a funnel in about 1 minute under vigorous mechanical stirring. A milky emulsion was formed immediately. The reaction continued for 1 hour. After cooling to room temperature, the white crude product solidified and was filtered and washed with water. The crude product was dried and recrystallized in hexanes/1-hexanol to the pure product. Yield: 38.2 g (60 %); mp 109.4-110.0 °C (reported¹⁰ 107-108 °C).

Synthesis of 1, 4- Bis(p-(p'-benzyloxyphenyl)isopropylidene)-phenoxy)benzophenone.

Compound **2.3** (8.000g, 25.1 mmol) and potassium carbonate (2.000 g, 14.7 mmol) were added to a solution of 100 mL DMAc and 100 mL toluene in a three neck round bottom flask equipped with a Dean Stark trap, nitrogen inlet and

outlet and a mechanical stirrer. The reaction was maintained at reflux for about 4 hours to remove water from the system by azeotropic distillation and toluene was finally removed. The solution was cooled down to room temperature and 4,4'-difluorobenzophenone (2.7411 g, 12.6 mmol) was added. The system was under reflux for about 24 hours. The salts were filtered and DMAc was removed by rotatory vacuum distillation to get a sticky yellow solution, which was poured into methanol under stirring to precipitate out a solid product. The product was washed with boiling methanol and filtered and dried under vacuum at 65 °C overnight. Yield : 10.0 g (98 %); mp 94.4-95.8 °C; ¹H NMR (400 MHz, CDCl₃): δ=7.78 (d, 4H, J=8.8 Hz), 7.30-7.45 (m, 10 H), 7.25 (d, 4H, J=8.8 Hz), 7.17 (d, 4H, J=8.8 Hz), 7.02 (d, 4H, J=8.8 Hz), 6.98 (d, 4H, J=8.8 Hz), 5.04 (s, 4H), 1.68 (s, 12H); FTIR (KBr): 3036 (Ar-H), 1652 (carbonyl), 1592, 1499 (C=C), 1241 (C-O-C) .

Elemental Analysis for C₅₇H₅₀O₅ Calc: C 84.00 H 6.18 O 9.82

Found: C 83.88 H 6.21

Synthesis of 4,4'-Bis[p-(p'-hydroxyphenyl)isopropylideneoxy]benzophenone.

Compound **2.6** (30.000g, 36.8 mmol) and sodium iodide (22.5 g, 150 mmol) were dissolved in 700 mL acetonitrile and heated to 82 °C under magnetic stirring and nitrogen protection. Trimethylsilyl chloride (20 mL, 156 mmol) dissolved in 100 mL acetonitrile was added dropwise. The reaction was kept under reflux for 30 hours. Then 100 mL water was poured in and the solution

was under reflux for one hour to complete the hydrolysis. The reaction was cooled down to room temperature and kept overnight. Then the solvent was removed to get a red solid, which was dissolved in chloroform and the red solution was washed with 10 % sodium thiosulfate until the red color (Iodine) disappeared. The chloroform solution was further washed with deionized water three times to remove inorganic salts, dried with sodium sulfate and taken to dryness. The byproduct benzyl iodide was removed by washing the product on a short silica gel column with hexanes and the product was eluted out with 2:1 (v/v) hexanes/ethyl acetate to get the pure product. Benzyl iodide can also be removed by dissolving the crude product in acetonitrile followed by exhaustive extraction with hexanes. The product was a pale yellow glassy compound. Yield : 20.0 g (86 %); mp 88.0-93.0 °C; ¹H NMR (400 MHz, CDCl₃): δ=7.77 (d, 4H, J=8.8 Hz), 7.23 (d, 4H, J=8.8 Hz), 7.01 (d, 4H, J=8.8 Hz), 6.96 (d, 4H, J=8.8 Hz), 6.76 (d, 4H, J=8.8 Hz), 5.30(s, 2H), 1.67 (s, 12H); FTIR (KBr): 3389 (OH), 1636 (carbonyl), 1589, 1497 (C=C), 1244 (C-O-C).

Elemental Analysis: C₄₃H₃₈O₅ Calc. C 81.36 H 6.03 O 9.82

Found C 81.15 H 6.07

Synthesis of cyclo-oligo(oxy-p-phenylene-isopropylidene-p-phenyleneoxy-p-phenylene-carbonyl-p-phenylene) (Scheme 2.5)

The typical synthetic procedure is as follows. To a three-neck 1L round bottom flask equipped with a Dean-Stark trap, nitrogen inlet-outlet and a mechanical stirrer were charged 500 mL DMAc and 230 mL toluene. The

system was azeotropically refluxed for 3-4 hours to remove water and the temperature was raised to 158 °C by distilling some toluene. 30 mL DMAc was taken from the flask to dissolve the extended bisphenol **2.8** (5.000 g, 7.88 mmol) and 4,4'-difluorobenzophen (1.719 g, 7.88 mmol). The solution was loaded into a 50 mL syringe and injected by a syringe pump at a rate of 1 mL/h into the flask with suspended potassium carbonate (2.613 g, 18.9 mmol). After about 60 hours of reaction, salts were filtered and the solvent was removed by a rotatory evaporator. The crude product was washed with water. The yield was quantitative. The crude product was dissolved in about 30 mL chloroform and precipitated in methanol to get a cyclic mixture. The insoluble cyclic dimer was obtained by washing the crude product with toluene. Yield 3.76 g (59 %); mp 386 °C (by DSC); ¹H NMR (400 MHz, CDCl₃): δ=7.71 (d, 8H, J=8.8 Hz), 7.24 (d, 8H, J=8.8 Hz), 6.99 (d, 8H, J=8.8 Hz), 6.97 (d, 8H, J=8.8 Hz), 1.71 (s, 12H); IR: 3064 (Ar-H), 2964 (CH₃), 1656 (CO), 1596, 1497 (C=C), 1244 (C-O-C), 1158, 1012, 925, 872, 839.

Reduction of 2.9 (n=1).

Macrocycle **2.9 (n=1)** (1.25 g, 1.6 mmol) was dissolved in 500 mL THF suspended with NaBH₄ (2.0 g, 52 mmol). The reaction was kept under nitrogen protection and reflux for about 36 hours. THF was removed by a rotatory evaporator to almost dryness and the product was precipitated in and washed with a large amount of water to get the reduced product. The product was dried in the vacuum oven over night above 60 °C. Yield: 1.06 g (84 %); mp 327.2-

330.2 °C (uncorrected). The reduced product is a mixture of diastereomers. ^1H NMR (400 MHz, CDCl_3): δ =7.28 (d, 8H, J=8.8 Hz), 7.17 (d, 8H, J=8.8 Hz), 6.93 (d, 8H, J=8.8 Hz), 6.88 (d, 8H, J=8.8 Hz), 5.82 (s, 2H), 1.63 (s, 12H).

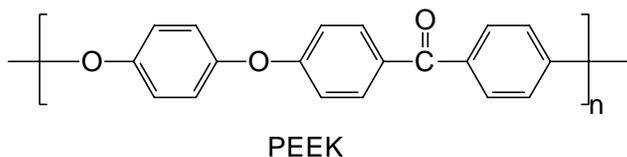
Synthesis of Cyclic Mixture by Linear Oligomer Approach.

To a one-neck round flask equipped with a magnetic stirrer, Dean-Stark trap and N_2 inlet-outlet were added 40 mL DMAc and 20 mL toluene. The solvent was azeotropically refluxed for three hours before K_2CO_3 (2.488 g, 18 mmol), 4,4'-difluorobenzophenone (2.1820 g, 10 mmol) and bisphenol-A (3.424 g, 15 mmol) were added. After 16 hours, toluene was distilled off and the reaction continued for 8 hours. After cooling down to room temperature, 4,4'-difluorobenzophenone (1.0910 g, 5 mmol) was added to the flask to make a slurry. This slurry was added to another refluxing flask with the same setup and containing 500 mL DMAc, 150 mL toluene and K_2CO_3 (0.691 g, 5 mmol), in three portions over a period of 36 hours. The reaction continued for another 24 hours. Solvent was removed on a rotatory evaporator. The solid was washed with water, dried and dissolved in 20 mL chloroform. The chloroform solution was poured into 200 mL methanol. The product was filtered and dried in a vacuum oven. Yield 5.45 g (89 %).

Chapter 3

Synthesis and Characterization of Macrocyclic Monomers for Poly(ether ether ketone)

3.1 Introduction



Poly(oxy-1,4-phenylene-oxy-1,4-phenylene-carbonyl-1,4-phenylene), commonly known as PEEK, is a commercial high performance polymer developed by ICI. This unique polymer is widely known for its excellent mechanical properties, thermal and environmental stabilities¹. The ether and carbonyl linkages in the chain give efficient packing and thus high crystallinity of PEEK, which is responsible for its excellent solvent resistance. PEEK is insoluble in common organic solvents. It is only soluble in strong protonating solvents such as sulfuric acid and methanesulfonic acid.

Rose and coworkers²⁻³ were the first to succeed in preparing high molecular weight PEEK from hydroquinone and 4,4'-difluorobenzophenone in

[1] May, R. "Encyclopedia of Polymer Science and Engineering", John Wiley & Sons Inc., New York, **1988**, Vol. 12, pp. 313-320.

[2] Rose, J. B.; Staniland, P. A. US Patent 4,320,224 (**1982**).

diphenyl sulfone at about 320 °C. Using the inert and high boiling point diphenyl sulfone solvent permits the application of reaction temperatures near the melting point of PEEK to prevent premature crystallization of the polymer. To overcome the synthetic difficulty due to poor solubility of PEEK, McGrath and his coworkers⁴ at Virginia Tech and Sogah and Risse⁵ at Dupont developed a low temperature synthetic method using 4,4'-difluorobenzophenone and substituted hydroquinone with a removable bulky t-butyl group to get an amorphous precursor polymer in conventional solvents such as DMSO. PEEK was then obtained after the t-butyl group was removed by retro Friedel-Crafts alkylation. However, the melting point of the resulting semicrystalline polymer was significantly lower than commercial PEEK, probably due to the incomplete de-t-butylation or side reactions. McGrath's group⁶ also developed a similar approach using 4,4'-difluorobenzophenone ketimine monomer instead of 4,4'-difluorobenzophenone to get poly(aryl ether ether ketimine), which was hydrolyzed to afford PEEK. The required ketimine to ketone transformation was

[3] Attwood, T. E.; Dawson, P. C.; Freeman, J. L.; Hoy, R. J.; Rose, J. B.;

Staniland, P. A. *Polymer* **1981**, 22, 1096.

[4] Mohanty, D. K.; Lin, T. S.; Ward, T. C.; McGrath, J. E. *Int. SAMPE Symp. Exhib.* **1986**, 31, 945.

[5] Risse, W.; Sogah, D. Y. *Macromolecules* **1990**, 18, 4029.

[6] Lindfors, B. E.; Mani, R. S.; McGrath, J. E.; Mohanty, D. K. *Makromol. Chem., Rapid Commun.* **1991**, 12, 337.

carried out under controlled heterogeneous hydrolysis conditions to give PEEK with melting point similar to commercial material.

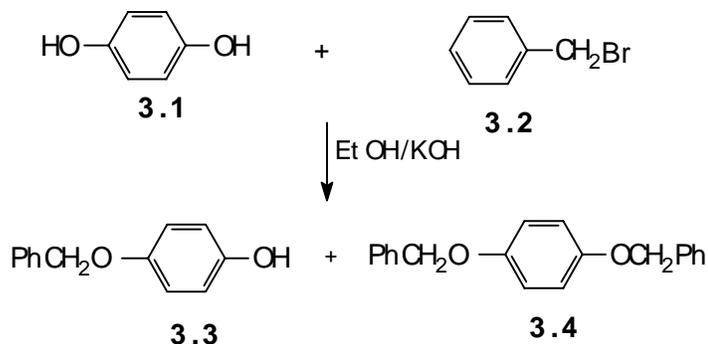
Despite its excellent combination of various desirable properties, it is very difficult to use PEEK as a matrix material for composites due to its high melt viscosity. A novel method has been developed by McGrath's group⁷ using a powder coating technique. In this method, micron size particles of PEEK are coated onto the carbon fiber. The final composite is made by sintering of the polymeric particles.

In recent years, the macrocyclic monomer technique has emerged as a novel method towards solving the processibility problem of high performance polymers. The advantages of using cyclic monomers include much lower melt viscosity and rapid ring-opening polymerization without generating volatile side products. These features are particularly valuable for the manufacture of advanced composite materials. It occurred to us that the macrocyclic precursor technique should also be applicable to semicrystalline systems such as PEEK. It would be an excellent solution to the tough processing problem of PEEK. This chapter is devoted to the synthesis and characterization of macrocyclic monomers for PEEK.

[7] Lyon, K. R.; Texier, A.; Gungor, A.; Davis, R. M.; McGrath, J. E. *Int. SAMPE Symp. Exhib.* **1992**, 37, 1301.

3.2 Synthesis of Precursors

Scheme 3.1



Following the same approach used in chapter 2, the monobenzyl ether of hydroquinone was synthesized first (Scheme 3.1). The interfacial reaction in aqueous media was tried first, which yielded a black solution because of oxidation of hydroquinone. The successful reaction was run in ethanol and the base used was potassium hydroxide. The key was to purge the reaction flask thoroughly with nitrogen to avoid oxidation of hydroquinone. The reaction was complete after about three hours. Upon cooling, much of the dibenzyl ether of hydroquinone byproduct crystallized from the solution. The system was neutralized with HCl solution in ethanol before the filtration of the precipitate. The crude product was washed with water to remove the excess hydroquinone. Pure product was obtained after recrystallization in hexanes/ethyl acetate. The melting point (120.4-122.0 °C) is close to reported value of 121-121.5 °C⁸. Its structure was further confirmed by IR and ¹H NMR spectroscopies (Figure 3.1).

[8] Rowe, W. *J. Org. Chem.* 1958, 23, 1622.

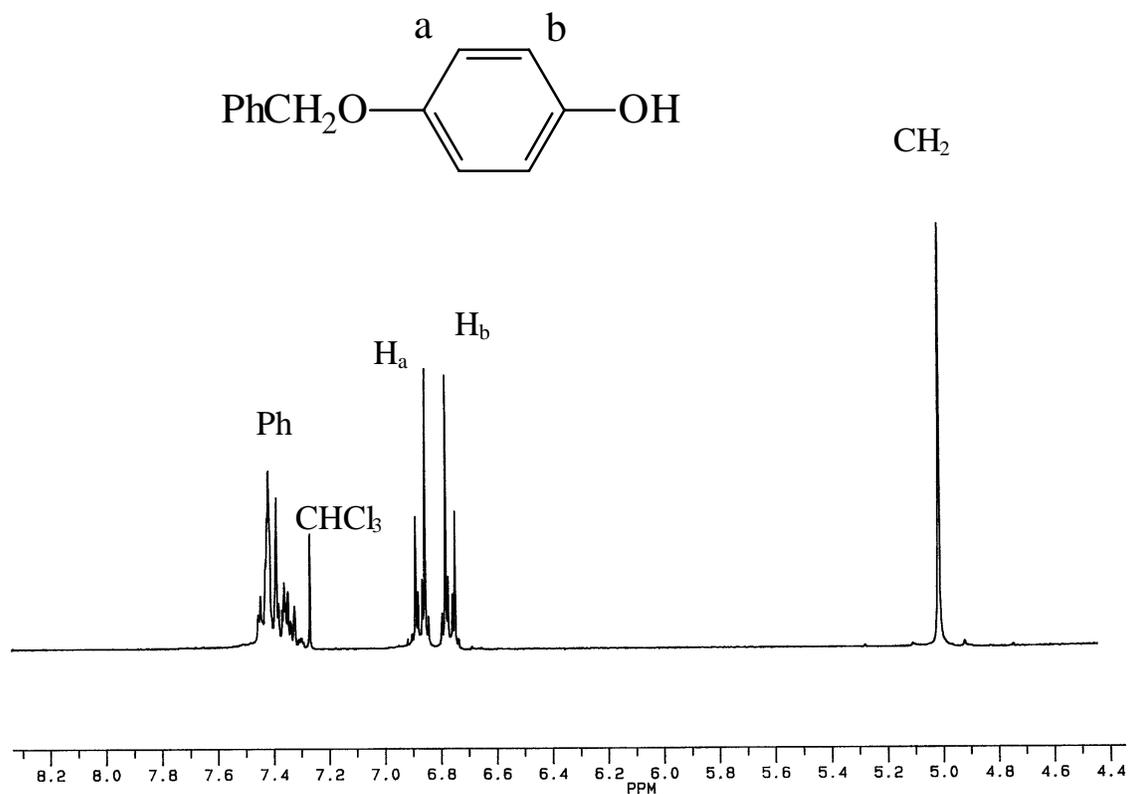
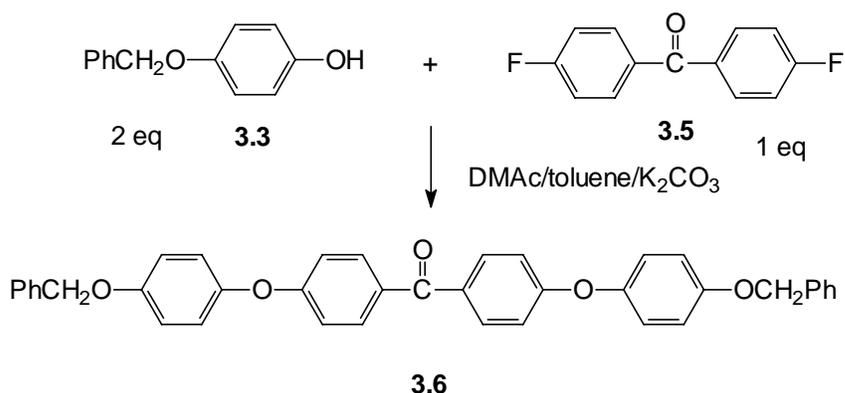


Figure 3.1. 270 MHz ^1H NMR spectrum of monobenzyl ether of hydroquinone in CDCl_3 .

Scheme 3.2



Next the monobenzyl ether of hydroquinone was reacted with half an equivalent of 4,4'-difluorobenzophenone to form new compound **3.6** (Scheme 3.2) using standard reaction conditions. This compound was purified by recrystallization in DMAc to afford a yield of 59 %. The structure of **3.6** was confirmed by NMR (Figure 3.2). Compound **3.6** is insoluble in acetone and acetonitrile. It is soluble in chloroform, hot DMAc and DMSO, however. This presents an unexpected solubility problem for the deprotection reaction. Deprotection of **3.6** with NaI/Me₃SiCl⁹ in acetone or acetonitrile was not successful. There was only very little reaction in acetone after several days. By that time the unstable Me₃SiI had probably decomposed. There was no detectable reaction in acetonitrile under similar reaction conditions. Although **3.6** can be deprotected by HBr/AcOH, the yield was poor (33 %) and the product was not pure. It was difficult to remove the side product.

[9] Olah, G. A.; Narang, S. C.; Gupta, B. G.; Malhotra, B.; *J. Org. Chem.* **1979**, 1247.

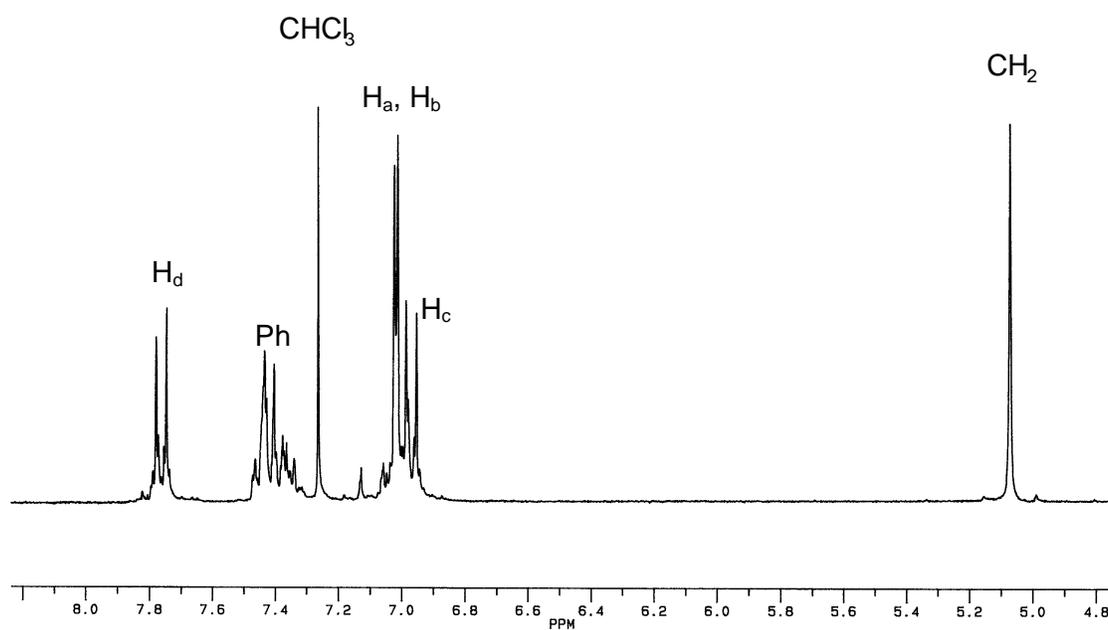
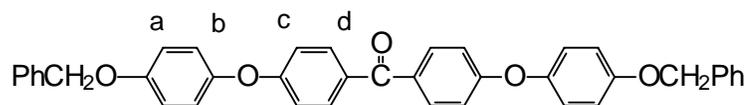
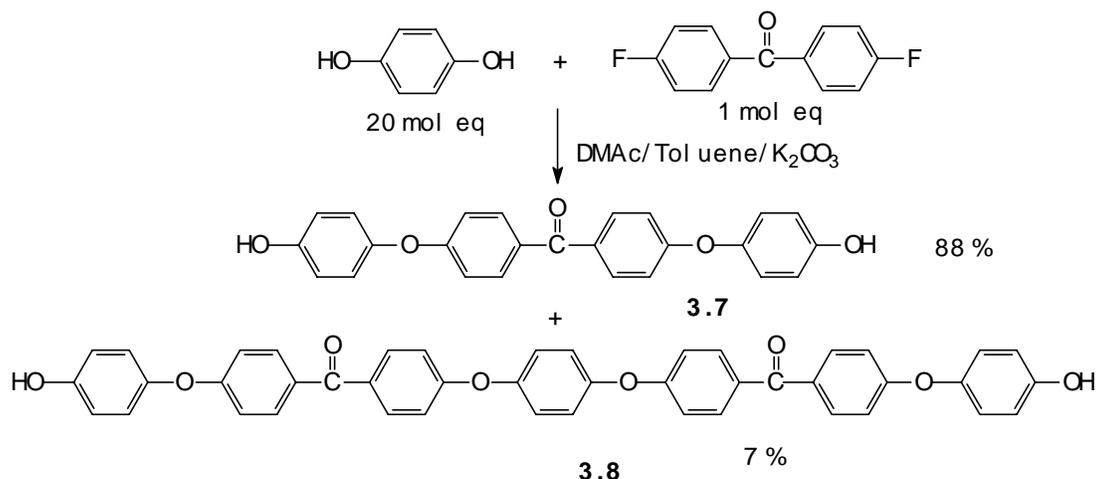


Figure 3.2. 270 MHz ^1H NMR spectrum of compound **3.6** in CDCl_3 .

Scheme 3.3



It was realized that the desired extended bisphenol **3.7** is probably a highly crystalline compound and its purification should be simpler. Therefore, it was synthesized directly using a one step approach. A large excess of hydroquinone was reacted with 4,4'-difluorobenzophenone to get the extended aromatic bisphenol, 4,4'-bis(4-hydroxyphenoxy)benzophenone (**3.7**, Scheme 3.3). Unlike the analogous long sulfone bisphenol previously reported from our lab¹⁰ the purification of **3.7** was quite easy because it is a crystalline compound. Fortunately, the large excess of hydroquinone, which is water soluble, was readily removed by washing the crude product with water. **3.7** is soluble in acetone and ethanol while the longer bisphenols are insoluble in these solvents. Therefore, **3.7** can be easily separated from the other products. Filtration through silica gel gave the pure product in a yield of 88 %. It can also be purified by recrystallization in methanol. **3.7** was also synthesized from inexpensive 4,4'-dichlorobenzophenone under similar reaction conditions. On TLC of the acetone

[10] Ganguly, S.; Gibson, H. W. *Macromolecules*, **1993** *26*, 2408. Compound **3**.

extraction there were two spots indicating some side reaction had taken place. This side reaction is very probably the type of single electron transfer reaction observed by Percec's group.¹¹⁻¹² After recrystallization in methanol, a yield of only 40 % was obtained. ¹H NMR analysis suggested that the product was not very pure.

Figure 3.3 shows the ¹H NMR spectrum of **3.7** synthesized from two different starting materials. Proton H_d, ortho to the carbonyl group, is located most downfield at $\delta=7.78$ ppm as a doublet. Proton H_c, which is coupled with H_a, appears as a doublet at $\delta=7.01$ ppm. Protons H_b and H_a are coupled with each other, appearing at $\delta=7.00$ and 6.91 ppm, respectively. The IR spectrum of compound **3.7** contains the characteristic broad hydroxyl peak at 3402 cm⁻¹, a carbonyl peak at 1644 cm⁻¹ and the ether stretch at 1244 cm⁻¹.

Despite the fact that hydroquinone was used in 900 % excess, small amounts of longer oligomers were formed due to the difunctionalities of the reactants. The long oligomeric bisphenol **3.8** was isolated in 7 % yield by extraction with DMAc. Compound **3.8** is actually a valuable compound for the

[11] Percec, V.; Clough, R. S.; Grigoras, M.; Rinaldi, P. L.; Litman, V. E.

Macromolecules **1993**, 26, 3650.

[12] Percec, V., Clough R. S., Rinaldi, P. L., Litman, V. E. *Macromolecules* **1991**,

24, 5889.

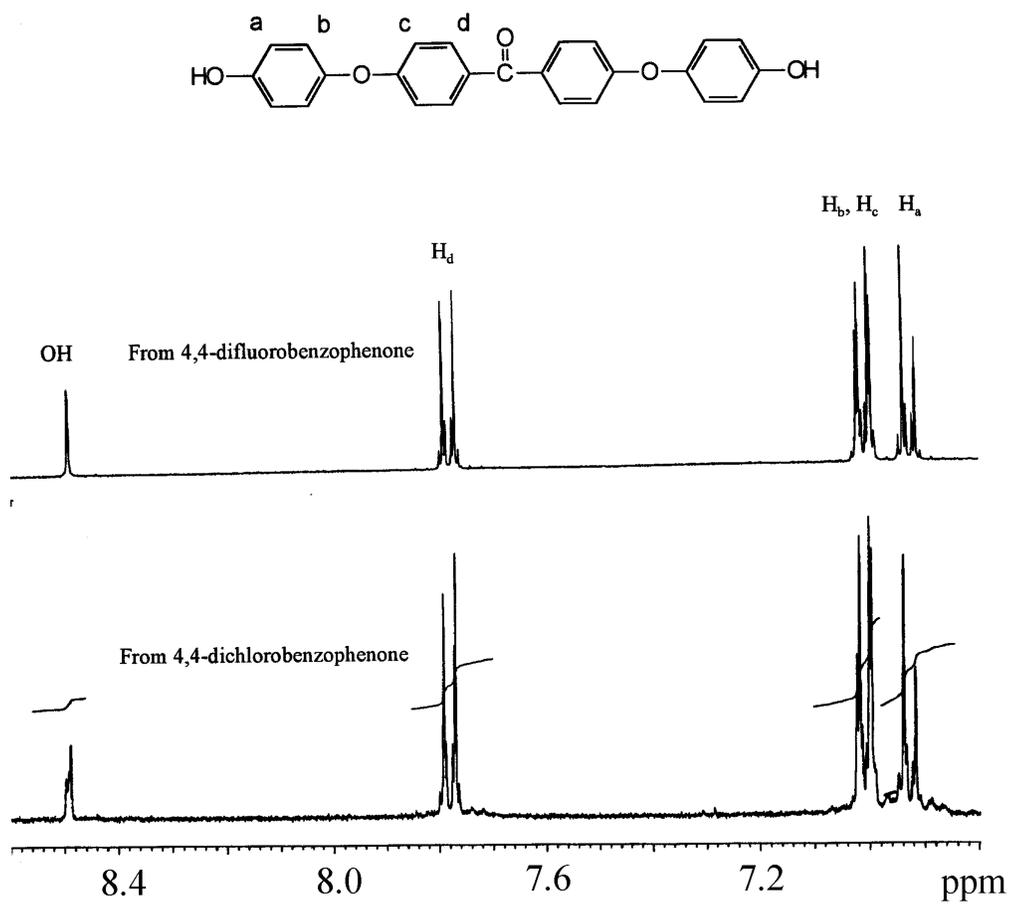
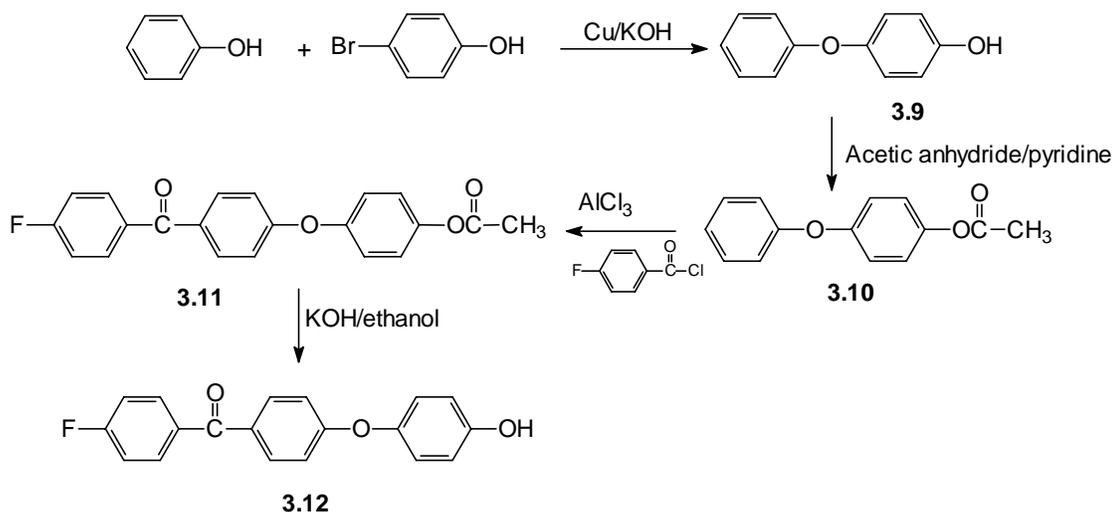


Figure 3.3. 400 ^1H NMR spectrum of compound 3.7 in acetone- d_6 .

synthesis of large sized macrocycles. Its ^1H - ^1H COSY NMR spectrum has a characteristic singlet peak for proton H_a due to the symmetric structure. Protons H_c and H_d are located downfield due to the electron withdrawing carbonyl groups. They are coupled with protons H_b and H_e , respectively. Protons H_f and H_g appear as two doublets, which are coupled with each other.

Scheme 3.4



The AA+BB type of cyclization is most common. Reports of cyclization using AB monomers are rare. We are also interested in using an AB monomer to compare with the AA+BB monomer approach. The AB monomer **3.12** was synthesized in four steps (Scheme 3.4). First 4-phenoxyphenol was prepared by Ullman reaction with copper as the catalyst. The yield was quite low (17 %). The product was isolated by vacuum distillation followed by recrystallization in toluene. Very pure product was obtained however as indicated by its narrow melting point (85-85.8 °C) and clean ^1H NMR spectrum (Figure 3.5).

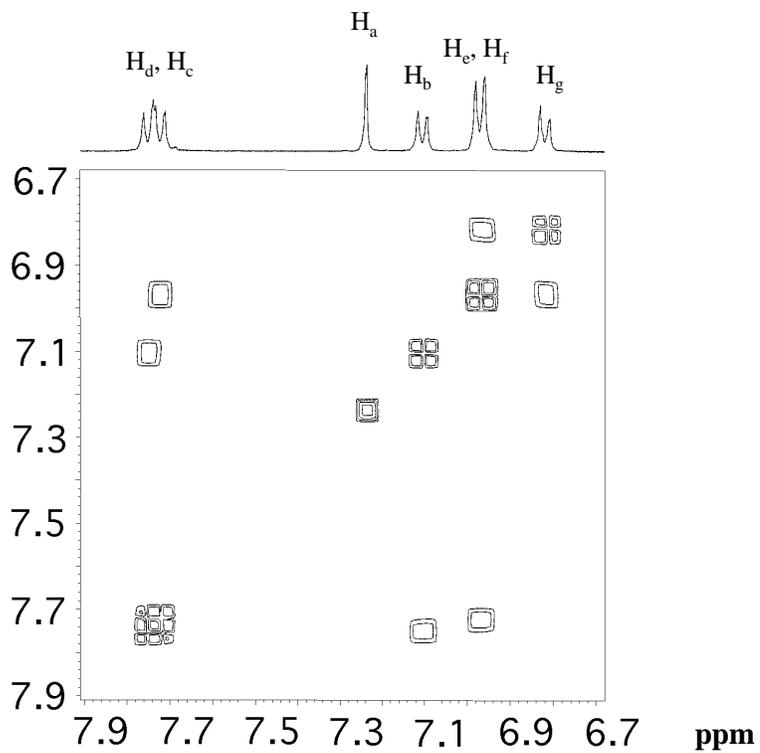
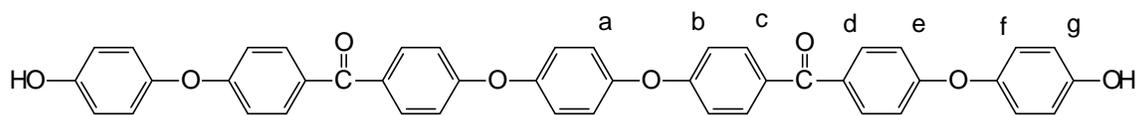
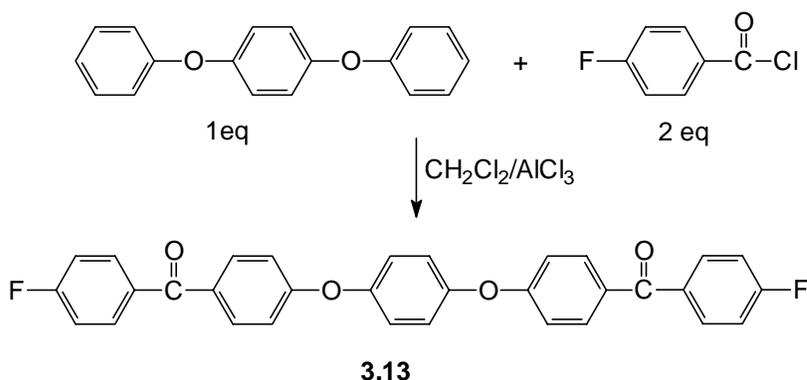


Figure 3.4. 400 MHz ^1H - ^1H COSY spectrum of compound **3.8**.

The hydroxyl group of 4-phenoxyphenol was then protected in ester form by reaction with acetic anhydride. The ester **3.10** is a liquid, which was used directly without purification except for being dried on a rotatory evaporator. Then the ester was reacted with one equivalent of 4-fluorobenzoyl chloride to form **3.11** through Friedel-Crafts acylation. Compound **3.11** was hydrolyzed with boiling KOH solution in ethanol to afford the final product **3.12**. There was no detectable hydrolysis reaction at room temperature. Substitution of fluoride with hydroxide was not observed under refluxing ethanol. The final product was obtained in 60 % yield by recrystallization in ethanol. The structure of **3.12** was confirmed by ^1H NMR (Figure 3.6).

Scheme 3.5



In order to get the large sized macrocycle efficiently, it is also necessary to use longer monomers. The difluoroaryl ketone compound **3.13** was obtained by Friedel-Crafts acylation of 4,4'-diphenoxybenzene with 4-fluorobenzoyl chloride using essentially the same procedure reported in the

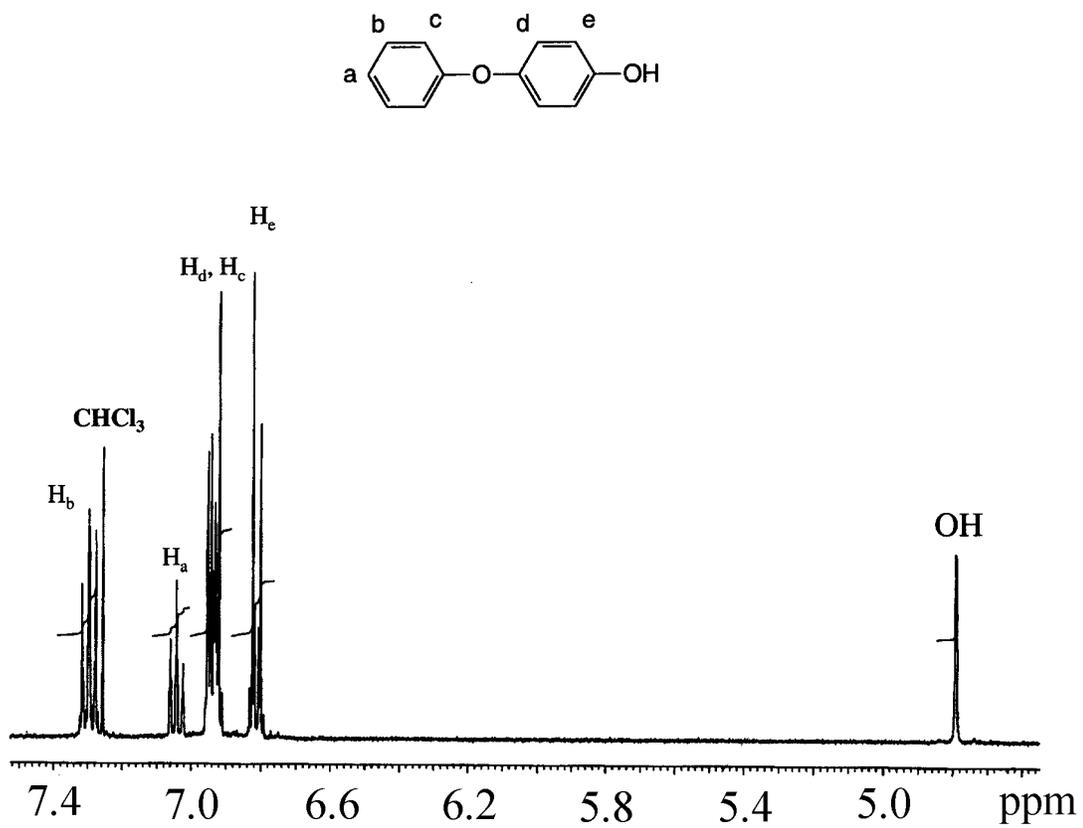


Figure 3.5. 400 MHz ¹H NMR spectrum of 4-phenoxyphenol in CDCl₃.

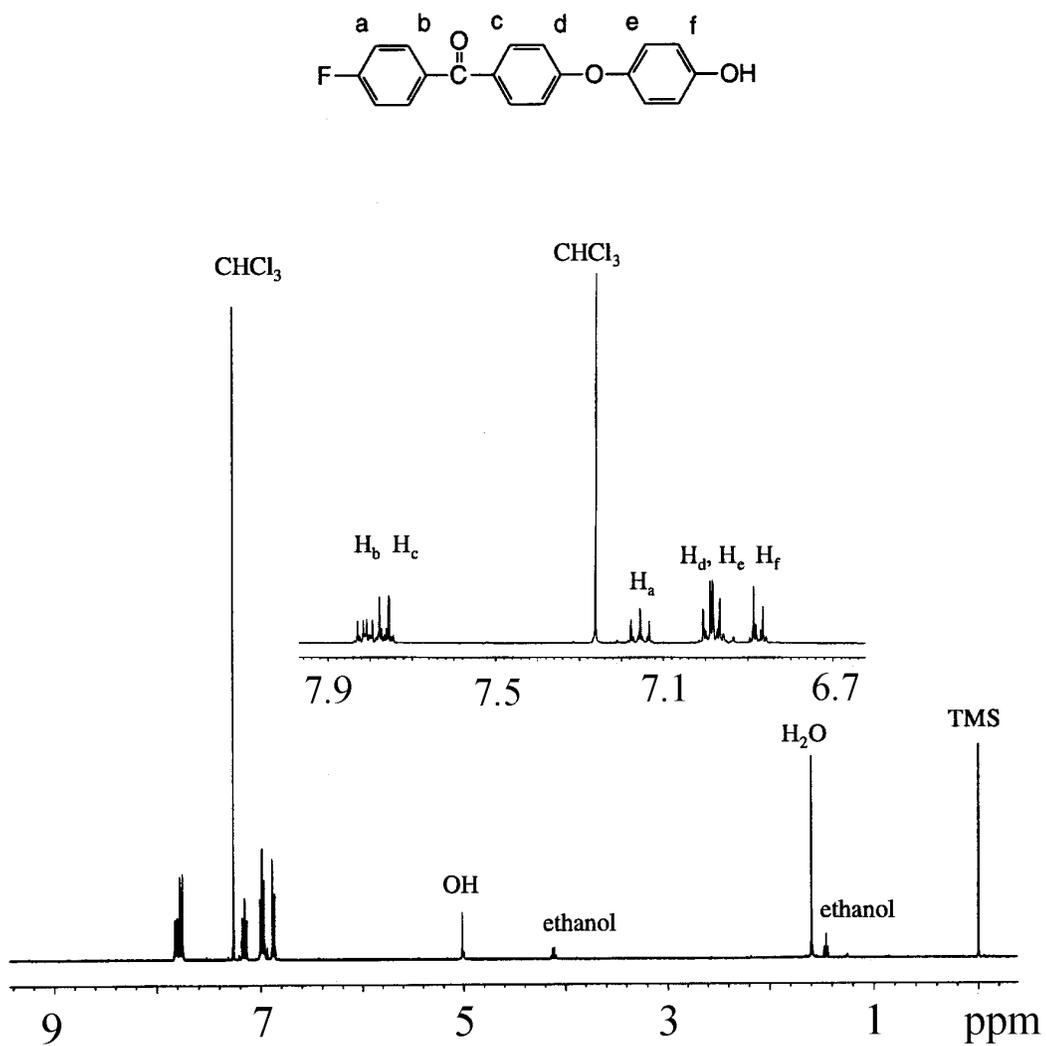
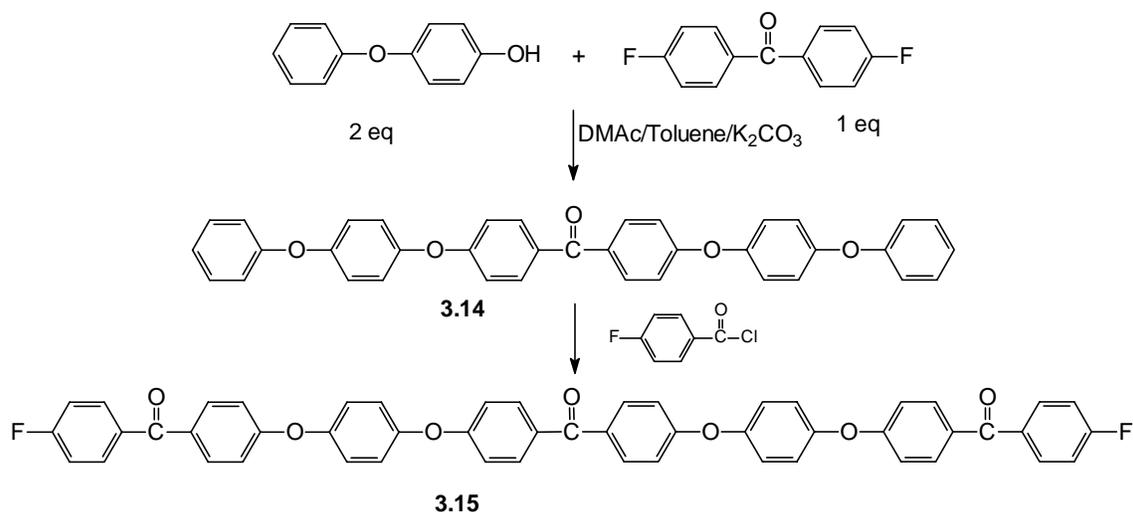


Figure 3.6. 400 MHz ^1H NMR spectrum of compound **3.12** in CDCl_3 .

literature.¹³ It was found that diphenoxybenzene is very reactive and the ferric chloride catalyst was unnecessary. The reaction was essentially quantitative. The final product was obtained by washing **3.13** with acetone. A small amount of Al₂O₃ was removed by precipitating the DMAc solution into 10 % HCl. The product can be further purified by recrystallization in DMAc. The melting point of this product was 232.1-235.3 °C, which is significantly higher than the reported value¹³ (223-225 °C). The yield was 98 %, also much higher than reported (75 %). The ¹H NMR spectrum of this compound is shown in Figure 3.7, which shows the characteristic singlet at δ=7.14 ppm. Other resonances are consistent with the structure.

Scheme 3.6



[13] Kricheldorf, H. R.; Delius, U.; Tonnes, K. U. *New Polymeric Mater.* **1988**, 1, 127.

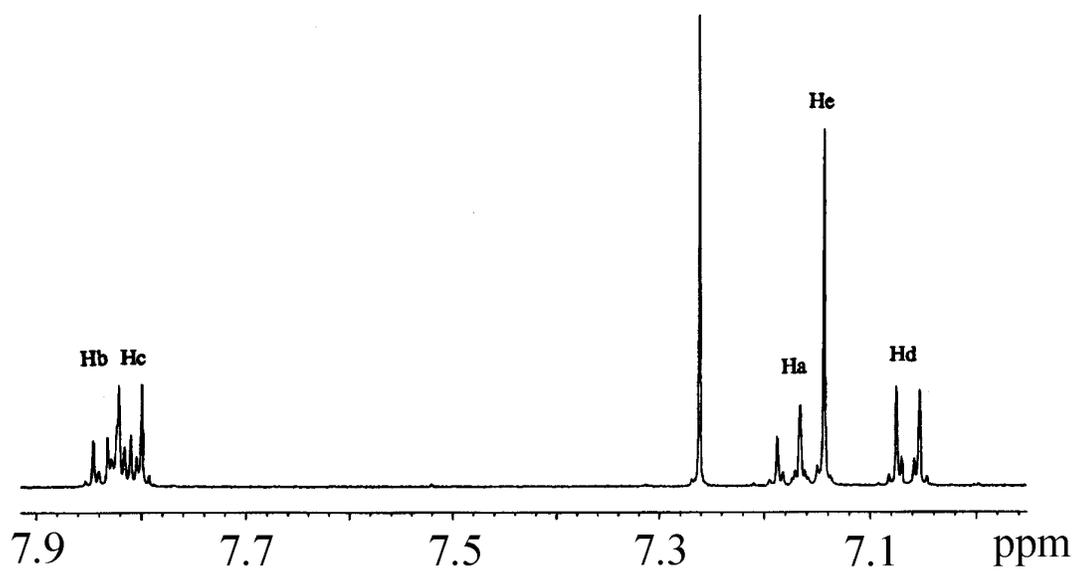
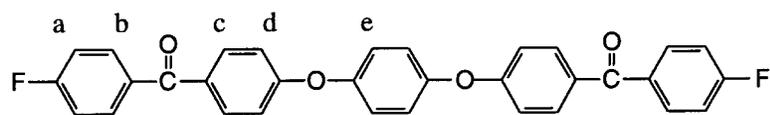


Figure 3.7. 400 MHz ¹H NMR spectrum of compound **3.13** in CDCl₃.

Longer difluoroaryl ketone **3.15** was obtained in two steps as shown in Scheme **3.6**. First, 4-phenoxyphenol was reacted with 4,4'-difluorobenzophenone to afford diphenoxy terminated **3.14** in almost quantitative yield, which was followed by Friedel-Crafts acylation to get the desired product. The key to this synthesis is protecting the reaction medium from water and using good anhydrous aluminum chloride. Trace amounts of excess starting material can be removed by washing the crude product with acetone. After recrystallization in DMAC, pure **3.15** was obtained in 96 % yield. Jonas and coworkers¹⁴ have reported synthesis of **3.15** using 4-fluorobenzoic acid in trifluoromethanesulfonic acid. The melting point (294 °C, detected by DSC) of this compound is almost the same as that reported in the literature and so is the melting enthalpy (137.3 J/g). Figure 3.8 shows the ¹H NMR spectrum of **3.15**. The spectrum was recorded at 100 °C in DMSO-d₆ because it is insoluble at room temperature. Thus the spectrum is broad and some peaks are overlapped. Nevertheless, the integrals of the spectrum are consistent with the structure.

[14] Jonas, A.; Legras, R.; Devaux, J. *Macromolecules* **1992**, *25*, 5841.

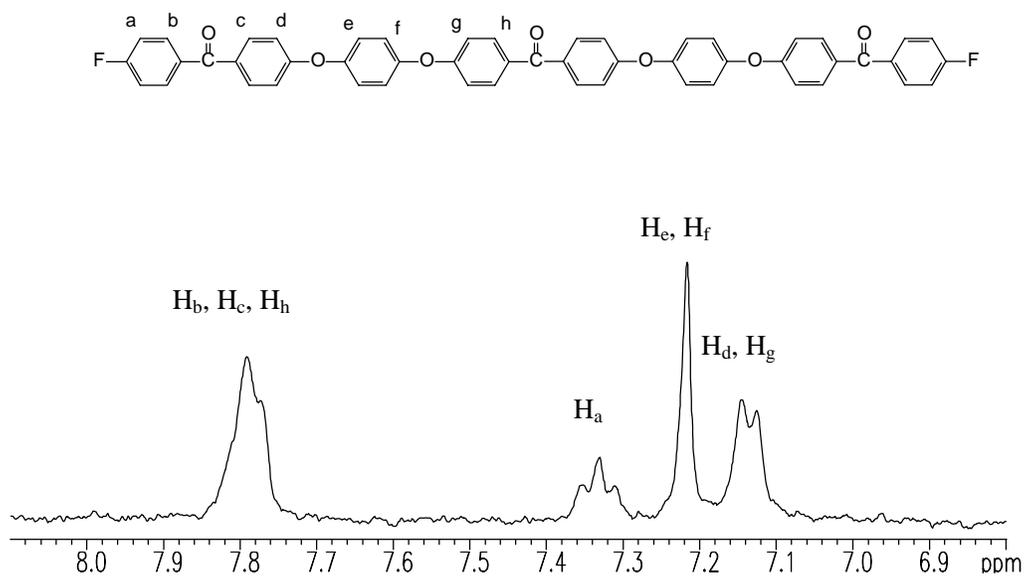
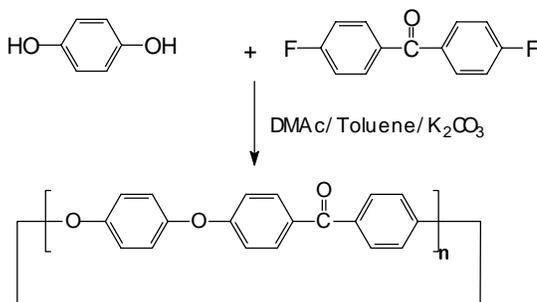


Figure 3.8. 400 MHz ^1H NMR spectrum of compound **3.15** in DMSO-d_6 at 100 °C.

3.3 Synthesis of Macrocyclic Monomers of Poly(ether ether ketone)

Scheme 3.7



3.16

A mixture of macrocycles was synthesized directly from hydroquinone and 4,4'-difluorobenzophenone under pseudo-high dilution conditions (Scheme 3.7). An equimolar solution of the two compounds was slowly injected into a reactor containing a refluxing mixture of DMAc and toluene and a 20 % excess of K₂CO₃. The temperature of the reaction was controlled by the fraction of toluene. During the reaction a precipitate was formed. After 64 hours of reaction, the precipitate was filtered off and the solvent was removed to get a cyclic product in 62 % yield. The ¹H NMR spectrum of the mixture showed no terminal groups, thus establishing its cyclic nature. Since the linear oligomers are expected to be insoluble in DMAc or other common organic solvents, this mixture is free from linear contamination. In the ¹H NMR spectrum of the cyclic mixture (Figure 3.9), there are 6 singlets around $\delta=7.18-7.30$ ppm, corresponding to peaks for macrocycles with up to 7 repeating units. The mixture consists of 46 % dimer, 26 % trimer and 20 % tetramer, with the rest being higher cyclic oligomers. Note that there is not any sign of aldol condensation side reaction which will be readily detected by NMR.

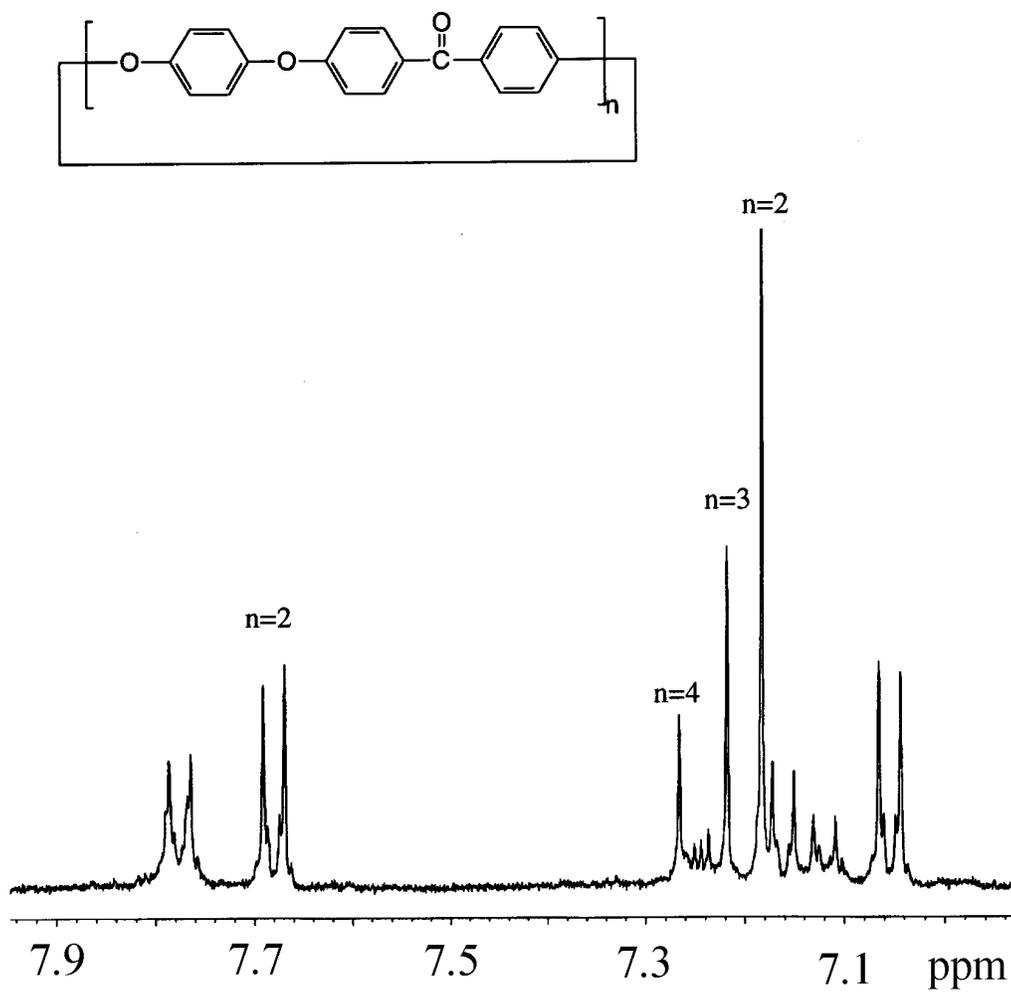
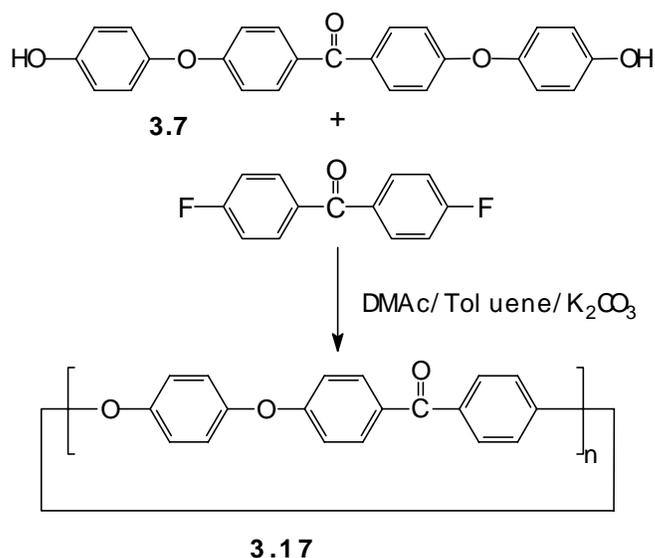


Figure 3.9. 400 MHz ^1H NMR spectrum of cyclic mixture **3.16** in DMSO-d_6 .

DSC indicated that the cyclic mixture has a melting point of 402 °C, which is too high for practical ring-opening polymerization. This melting point was confirmed by visual observation of the formation of clear liquid in the melting point apparatus. The cyclic dimer is less soluble in chloroform. After extracting the crude product with some chloroform, the amount of the dimer was reduced to 11 %. The melting point was lowered to 296 °C, which is in the appropriate range for ring-opening polymerization. However, the total cyclic yield was reduced to only 20 %.

Scheme 3.8



The cyclization reaction of the extended bisphenol **3.7** and one equivalent of 4,4'-difluorobenzophenone was carried out under similar high dilution conditions (Scheme 3.8). According to ^1H NMR spectrum (Figure 3.10), the mixture was composed of 68 % cyclic dimer, 3 % trimer, 17 % tetramer, 8 % pentamer and 4 % hexamer. Note that the formation of the trimer and pentamer

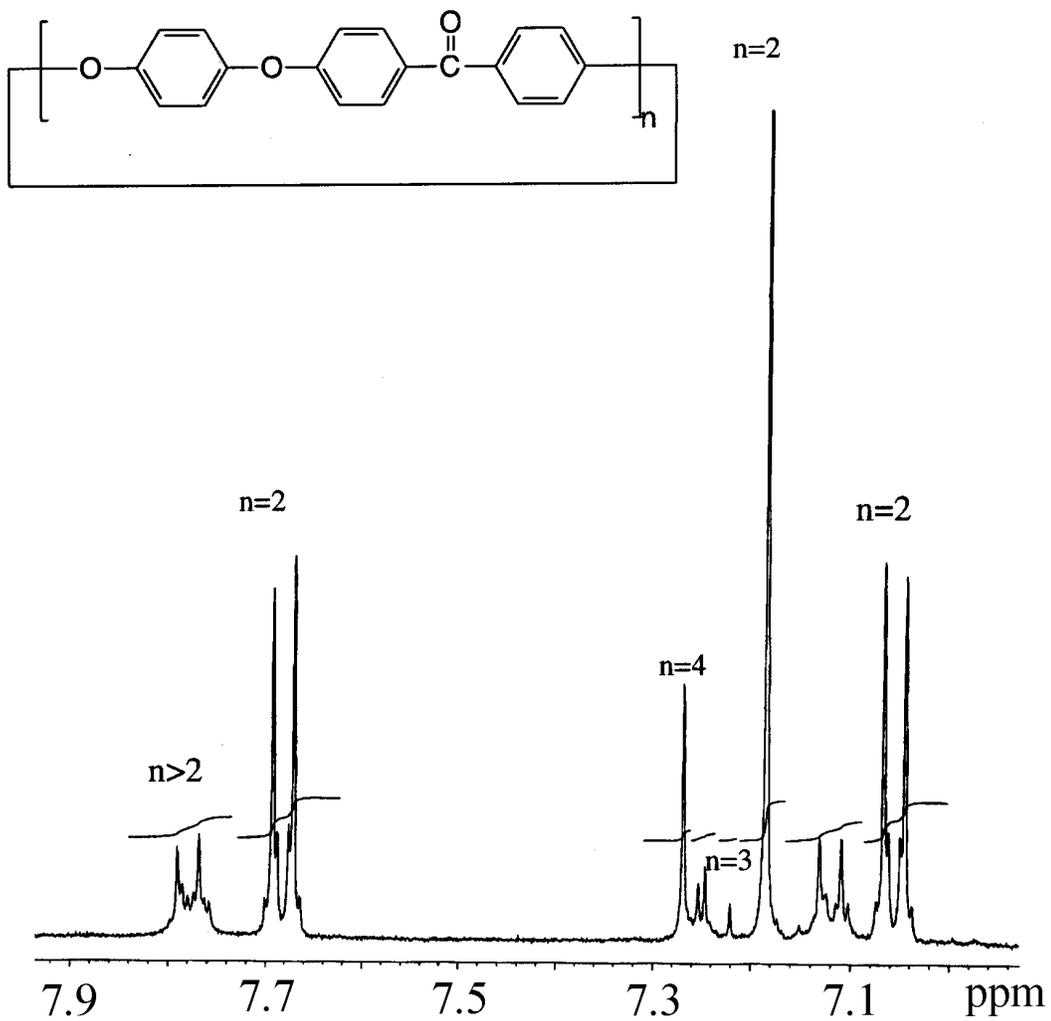
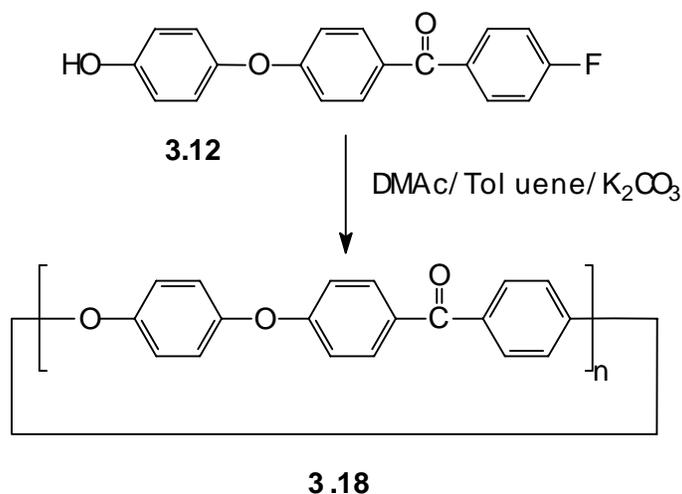


Figure 3.10. 400 MHz ^1H NMR spectrum of cyclic mixture of **3.17** in DMSO-d_6 .

is due to the ether exchange backbiting reaction, but only to a small extent. The distribution is obviously different from that of the mixture from the one step method. This mixture is also inappropriate for the ring-opening polymerization in the melt state due to high amount of cyclic dimer.

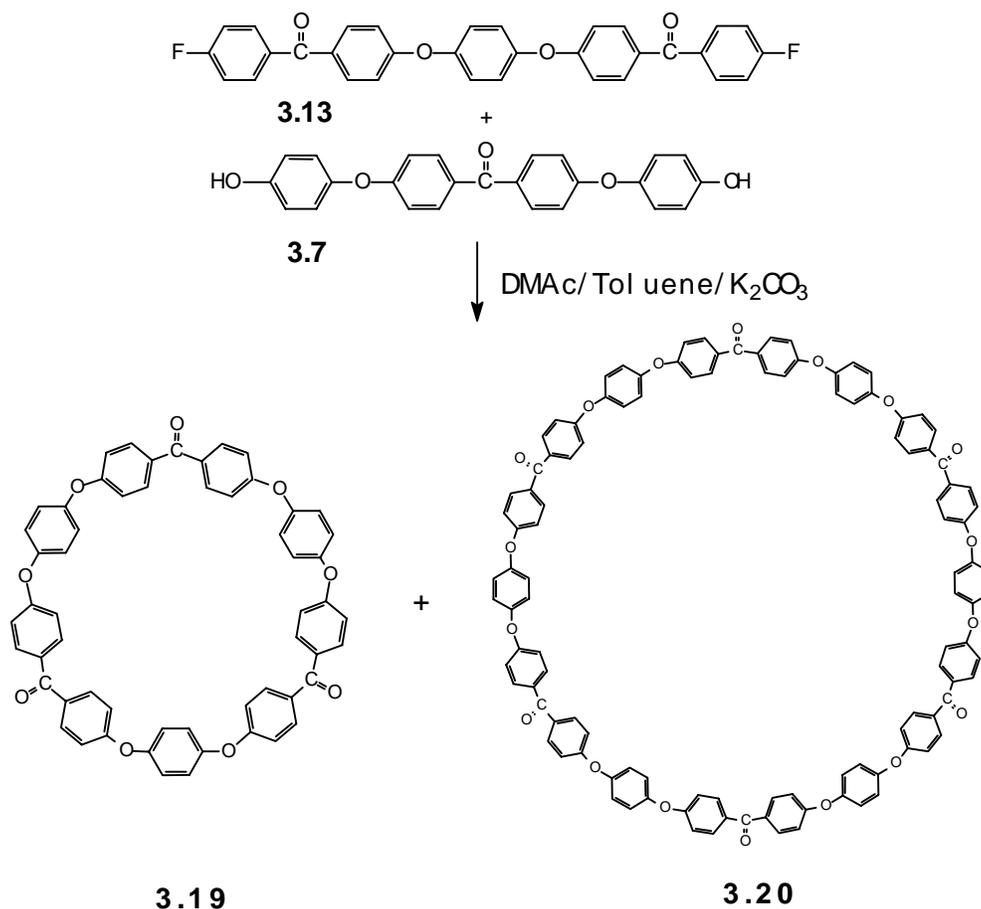
Scheme 3.9



The synthesis of the cyclic PEEK mixture was also carried out using AB monomer **3.12** (Scheme 3.9). It was quite a surprise that the total cyclic yield was low (35 %). Again the cyclic dimer was predominant (34 %) in the mixture.

From the above results, it is evident that the amount of cyclic dimer has to be reduced in order to get a mixture with appropriate melting point. Fortunately, the cyclic distribution is kinetically controlled based upon our previous study. Longer starting materials can be used to get a mixture composed of predominantly the large sized macrocycles.

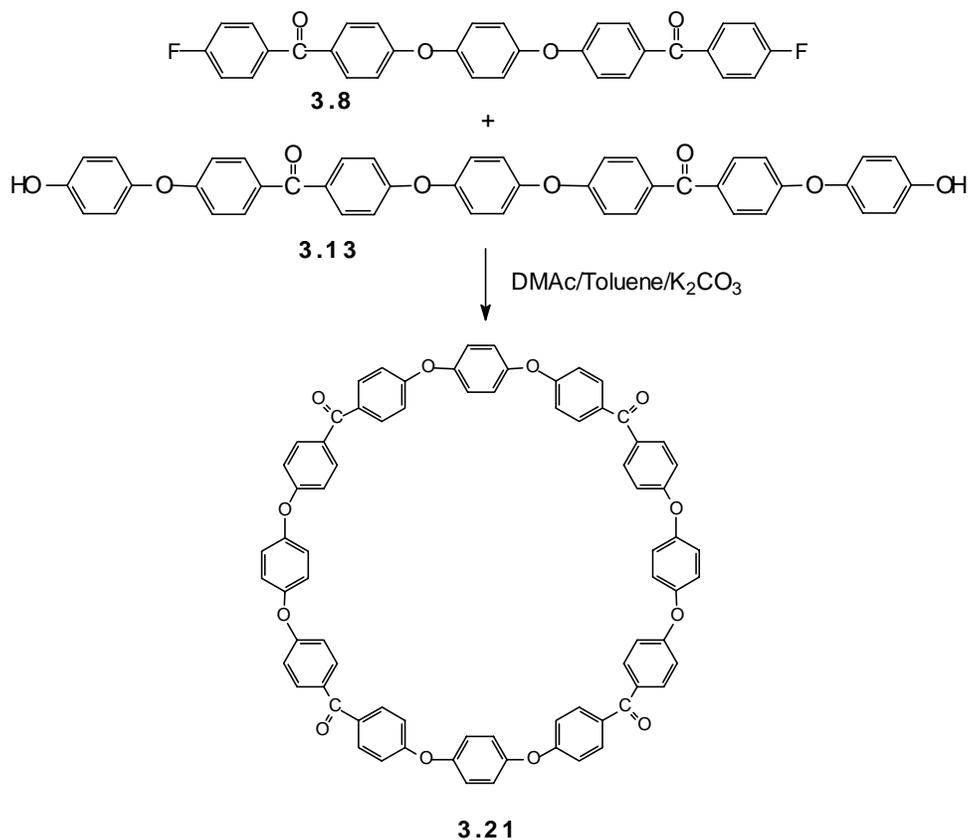
Scheme 3.10



Thus, a mixture of macrocycles consisting of mainly trimer and hexamer was synthesized using the extended bisphenol **3.7** and difluoroaryl ketone **3.13** under similar reaction conditions (Scheme 3.10). The syringe pump technique was not used because **3.7** is nearly insoluble in the solvent at room temperature. Instead the high dilution condition was maintained by adding equivalent amounts of monomers in four portions over a period of 36 hours. The cyclic mixture was obtained by exhaustive extraction with chloroform. On a small scale the yield was 70 %. The reaction was scaled up to about 15 grams and the yield was increased to 75 % because of less mechanical loss. According to the ¹H NMR

spectrum (Figure 3.11), the mixture consists of 83 % of 45-membered cyclic trimer **3.19** and 17 % of 90-membered cyclic hexamer **3.20**. Higher cyclic oligomers were not observed again due to the limited solubility of the linear PEEK precursors in DMAc. There is no end group present by ^1H NMR spectroscopy, establishing the cyclic nature of the mixture. According to RP-HPLC analysis (Figure 3.12), there were small amounts of cyclic dimer, tetramer and pentamer present in the mixture. The formation of these cyclics can be explained by the backbiting cyclization reaction. This result further confirms previous indications that the cyclic distribution is kinetically controlled and the backbiting ether exchange reaction is minimal.

Scheme 3.11



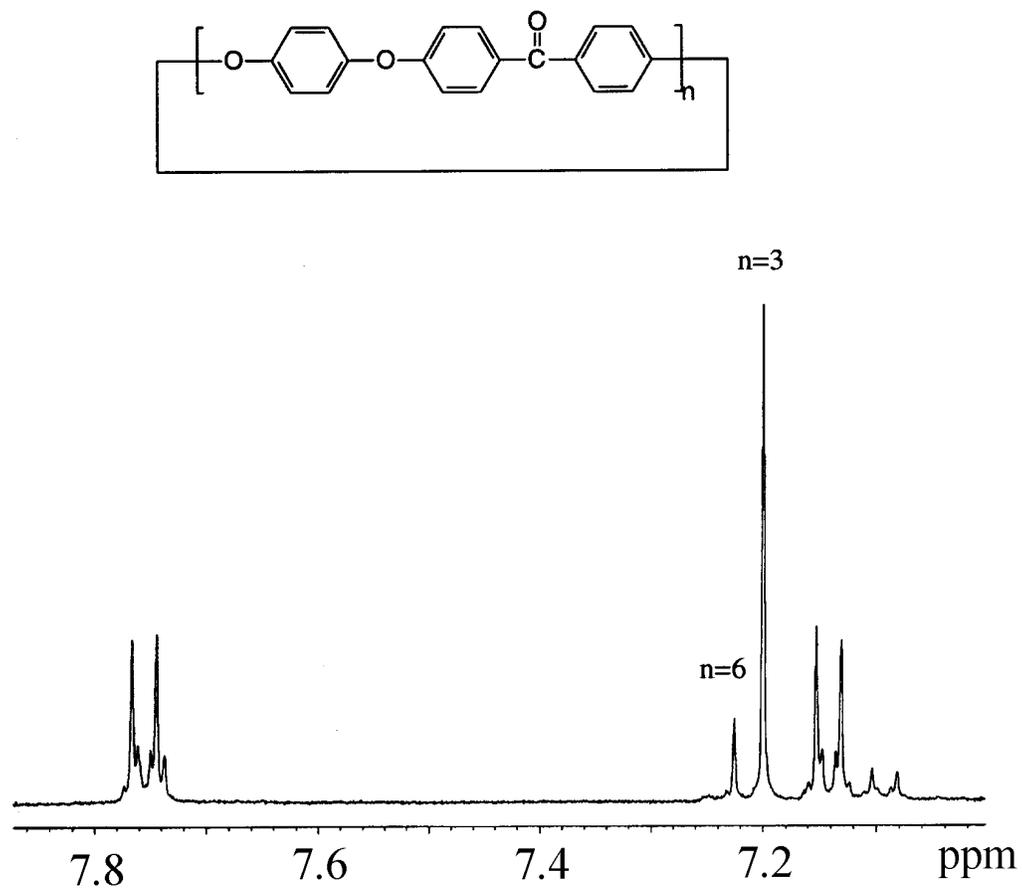


Figure 3.11. 400 MHz ^1H NMR spectrum of cyclic mixture of **3.19** and **3.20** in DMSO- d_6 .

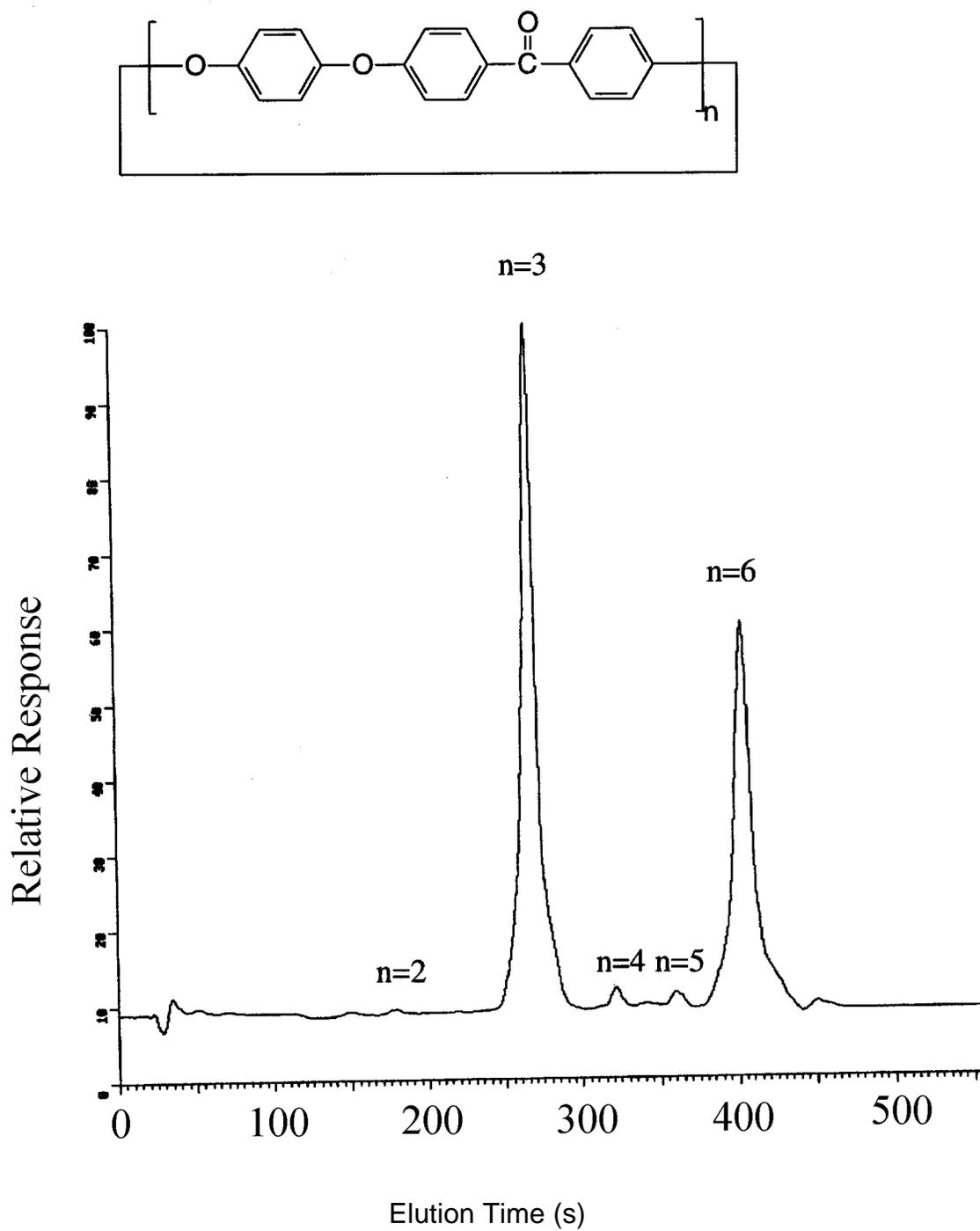
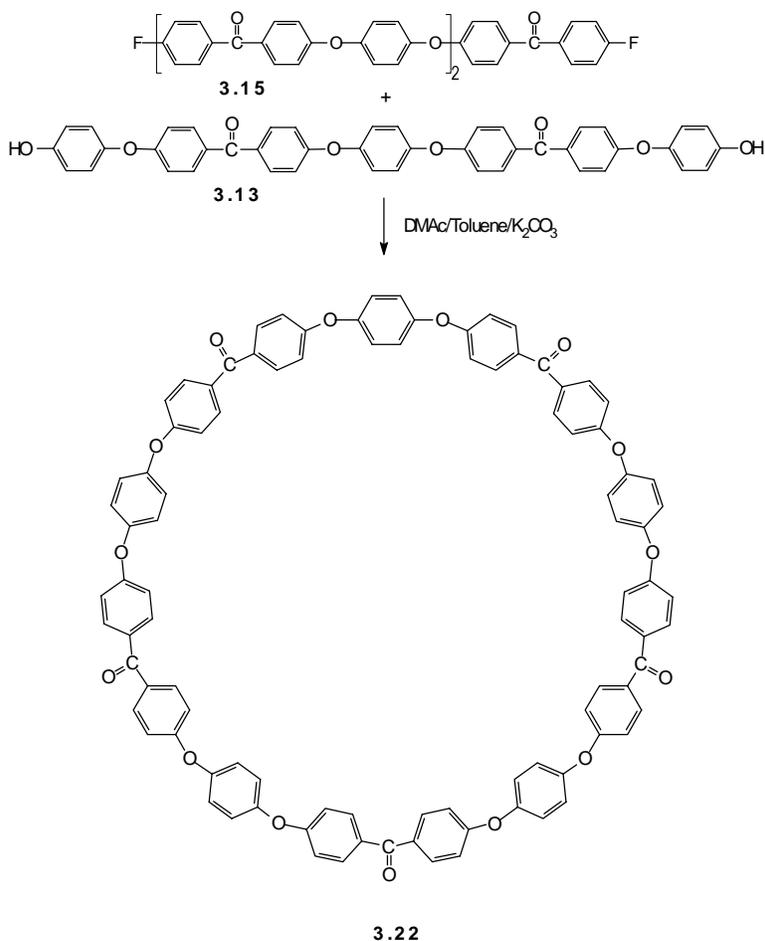


Figure 3.12. RP-HPLC chromatogram of cyclic mixture of **3.19** and **3.20**.

The synthesis of the 60-membered macrocycle **3.21** was accomplished by using longer bisphenol **3.13** and difluoroaryl ketone **3.8** (Scheme 3.11) under more dilute conditions (total reaction concentration 1.9 mM). The reactants were added batchwise. Again, the product was obtained by exhaustive extraction with chloroform. The cyclic yield was 66 %. The formation of the double sized macrocycle, i. e., the 120-membered macrocycle, was not observed. There were very small amounts of dimer and trimer as observed in the RP-HPLC chromatogram (Figure 3.13).

Scheme 3.12



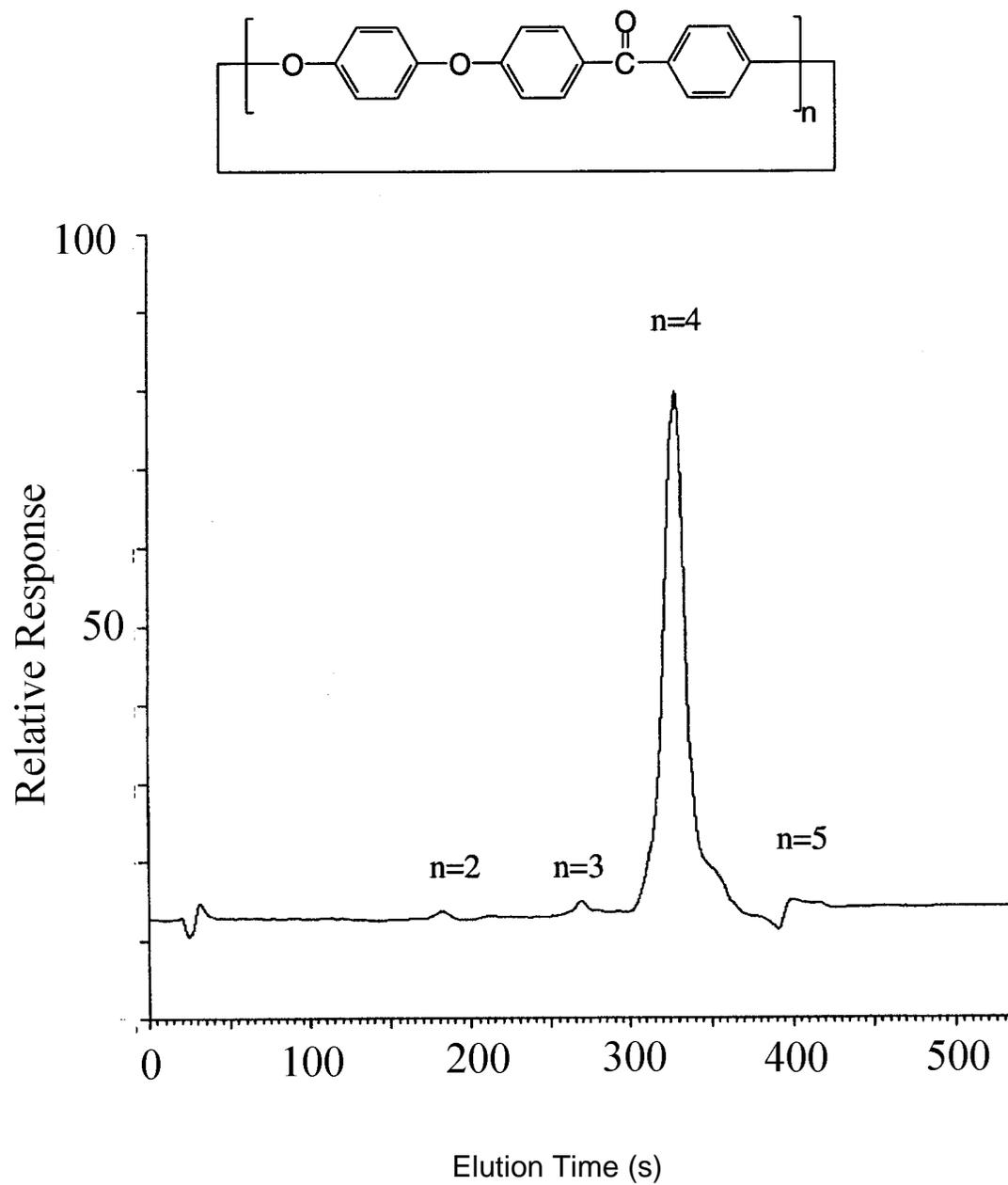


Figure 3.13. RP-HPLC chromatogram of macrocycle **3.21**.

The 75-membered pentamer **3.22** was obtained by combination of two long monomers (Scheme 3.12) using even more highly dilute reaction conditions (total concentration 1.7 mM). The isolated cyclic yield was 55 %, surprisingly high considering the size of the macrocycle. However, the product contains significant amounts of cyclic tetramer and hexamer as detected by RP-HPLC (Figure 3.14). This is because the reactive end group has difficulty finding another reactive end group. Instead it backbites in the middle of chain to form the small sized macrocycle.

3.4 Characterization of the Macrocycles

The isolation of the cyclic dimer (**3.17**, $n=2$) was accomplished by recrystallization of the crude product **3.17** in hot DMSO, which gave the pure compound in 27 % yield. The cyclic tetramer (**3.17**, $n=4$) was obtained directly from the reaction and further purified by recrystallization in THF. Isolation of the pure cyclic pentamer was not successful either by column chromatography or recrystallization.

The IR spectrum of the 30-membered cyclic dimer is shown in Figure 3.15. The IR spectrum indicates the carbonyl group at 1655 cm^{-1} and the ether group at 1225 cm^{-1} . The carbonyl absorption is quite weak, probably because of the symmetric structure of the macrocycle. Compared with the model linear compounds **3.7** and **3.8**, the carbonyl peak of the dimer is located at a higher

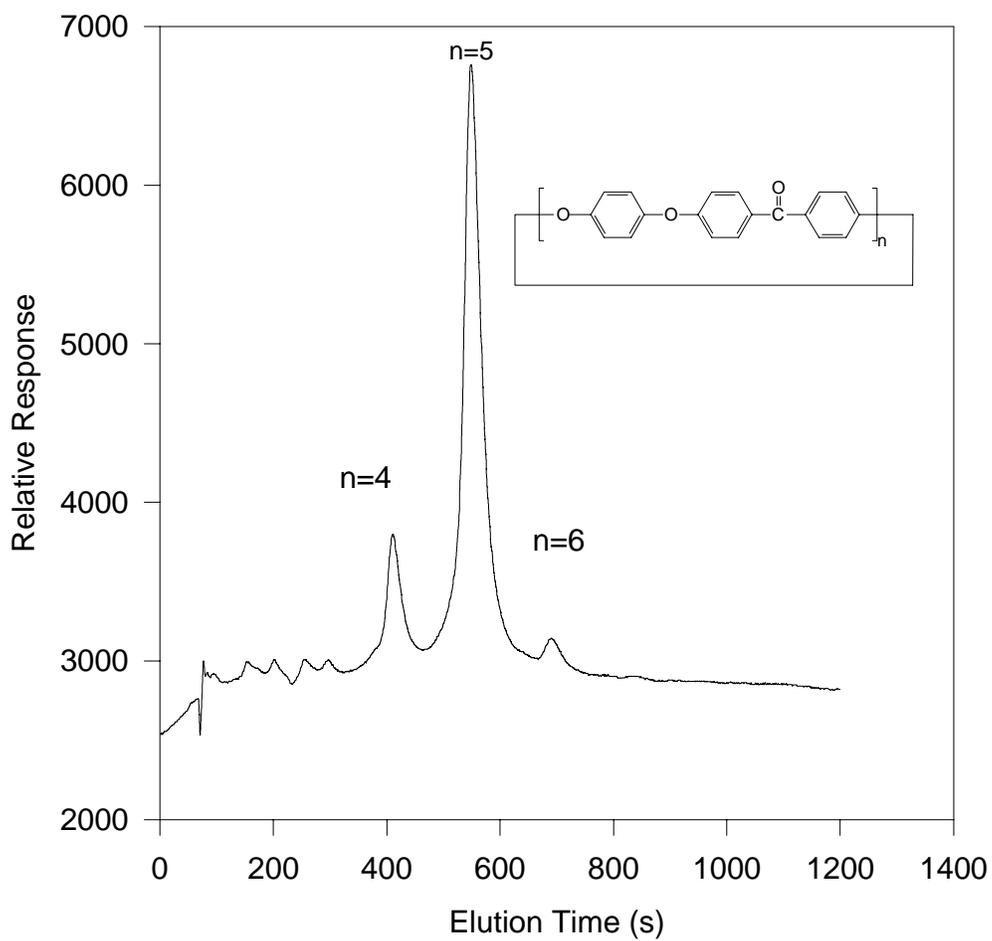


Figure 3.14. RP-HPLC chromatogram of Cyclic mixture **3.22**.

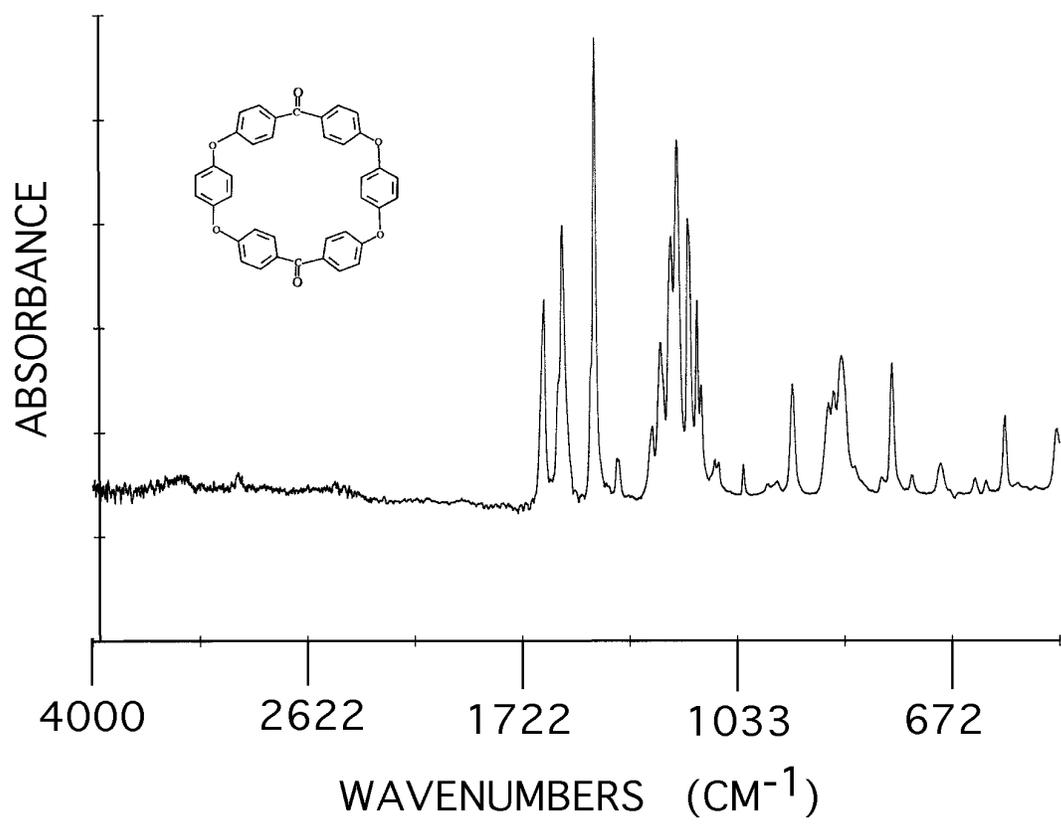


Figure 3.15. IR spectrum of macrocyclic dimer.

wave number. This is due to less conjugation of the carbonyl group with the phenyl groups probably because of non-coplanarity¹⁵.

This can also be seen in its proton NMR spectrum (Figure 3.16), which is quite simple due to the highly symmetric structure of cyclic dimer. The proton H_a, ortho to carbonyl group, is located downfield at $\delta=7.66$ ppm, which is lower than the chemical shifts ($\delta=7.76$ ppm) of a proton ortho to carbonyl in the linear compound **3.7**. The chemical shift of a phenyl proton is sensitive to the electron withdrawing ability of a substituent ortho to it, which develops a partial positive charge at the ortho position. The more electron withdrawing, the higher the chemical shift. Therefore, the lower chemical shift of H_a in the macrocycle can also be attributed to the reduced conjugation of the carbonyl group with the phenyl system. The other doublet located at $\delta=7.04$ ppm is due to proton H_b and the singlet at $\delta=7.16$ ppm is assigned to proton H_c. No terminal proton was detected in the spectrum, clearly indicating its cyclic structure.

Along with other large sized macrocycles, the cyclic dimer showed 7 peaks in the ¹³C NMR spectrum (Figure 3.17), which is consistent with their cyclic structure. The assignment of the peaks was made possible by a HETER-COSY experiment.

[15] R. M. Silverstein, G. C. Bassler, T. C. Morrill, "Spectrometric Identification of Organic Compounds", 4th ed., John Wiley & Sons, New York, **1981**, pp. 117-119.

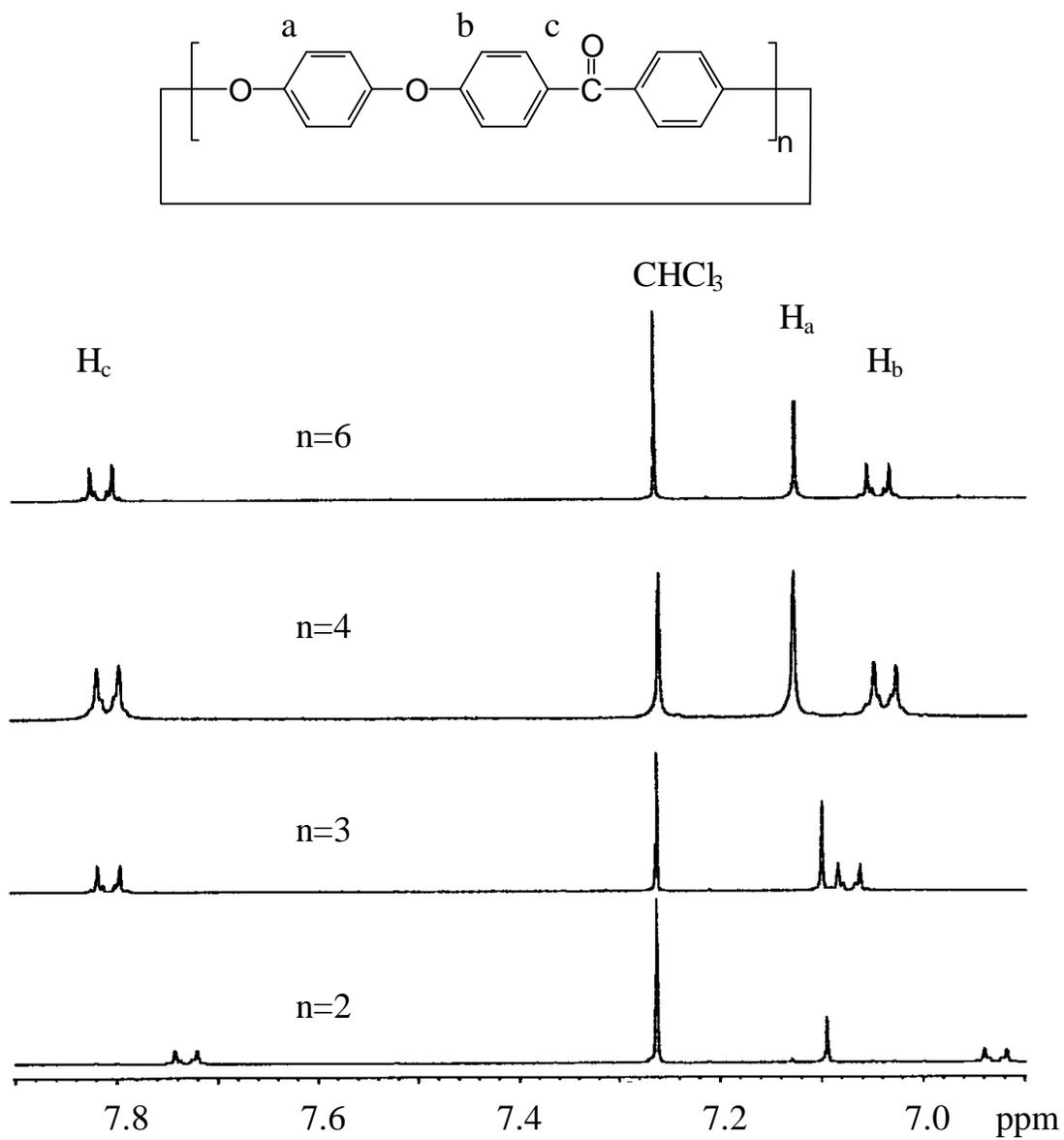


Figure 3.16. 400 MHz ^1H NMR spectra of pure macrocycles in CDCl_3 .

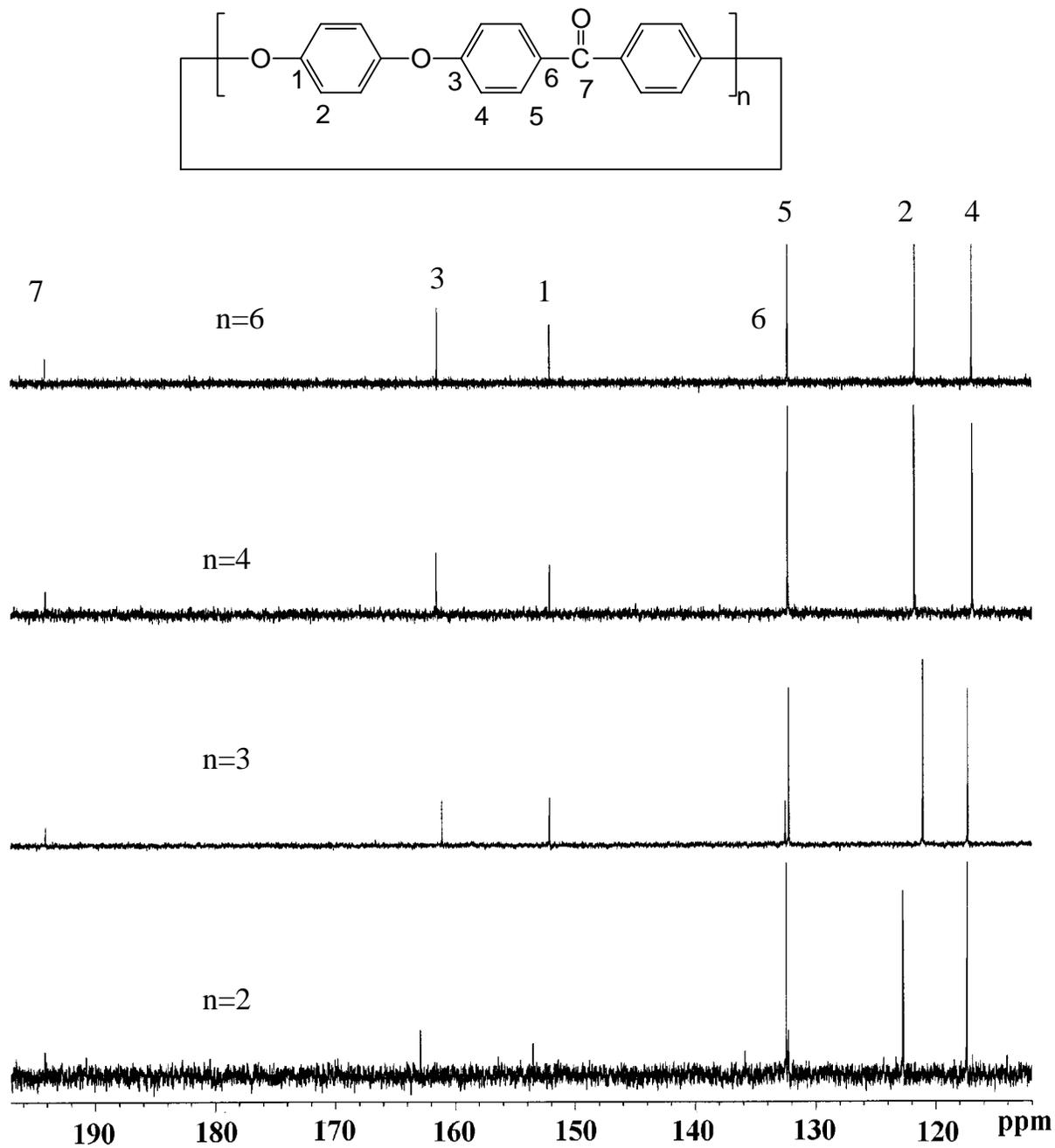


Figure 3.17. 100 MHz ^{13}C NMR spectra of pure macrocycles in CDCl_3 .

The ring size was determined to be 30 atoms based on the FABMS spectrum. The quasimolecular ion peak at 577.1 ($[M+H]^+$) exactly matches its calculated molecular weight.

The macrocycle is only slightly soluble in acetone, chloroform and DMSO. No melting was observed by DSC up to 420 °C, while the linear PEEK has a melting peak at 334 °C. The low solubility and infusibility can be attributed to the high rigidity of the macrocycle.

The TGA thermogram of the cyclic dimer (Figure 3.18) shows 5 % weight loss at 434 °C in air, and 442 °C in nitrogen. These temperatures are lower than those of PEEK. Notably the char yield is almost zero in nitrogen atmosphere, quite different from other aromatic macrocycles we have synthesized so far. Therefore, it is believed the weight loss is not due to decomposition, but to sublimation of the macrocycle at high temperature.

The X-ray structure of the macrocycle is shown in Figures 3.19-21. The crystal space group is P-1 with unit cell parameters $a=12.480$, $b=14.431$, $c=14.6287$ Å; $\alpha=99.348$, $\beta=90.173$, and $\gamma=94.830^\circ$. Detailed X-ray structure data is listed in Appendix B. The macrocycle adopts two slightly different conformations in the crystal (A and B). There are 4/3 acetone solvent molecules per macrocycle. The acetone molecule sitting above and below the A macrocycle is ordered and the acetone molecule sitting above the B macrocycle is disordered. The macrocycle adopts a quite rigid and relatively flat open conformation as can be seen from side view (Figure 20). The transannular

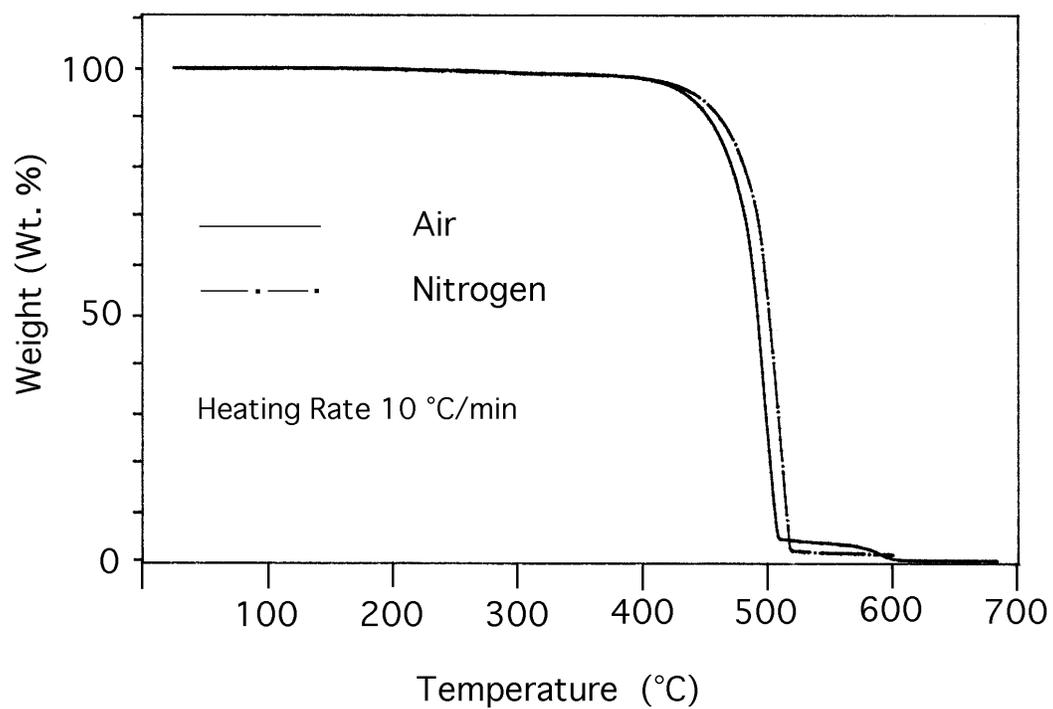
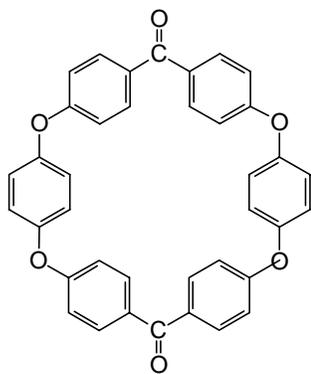


Figure 3.18. TGA thermograms of macrocyclic dimer.

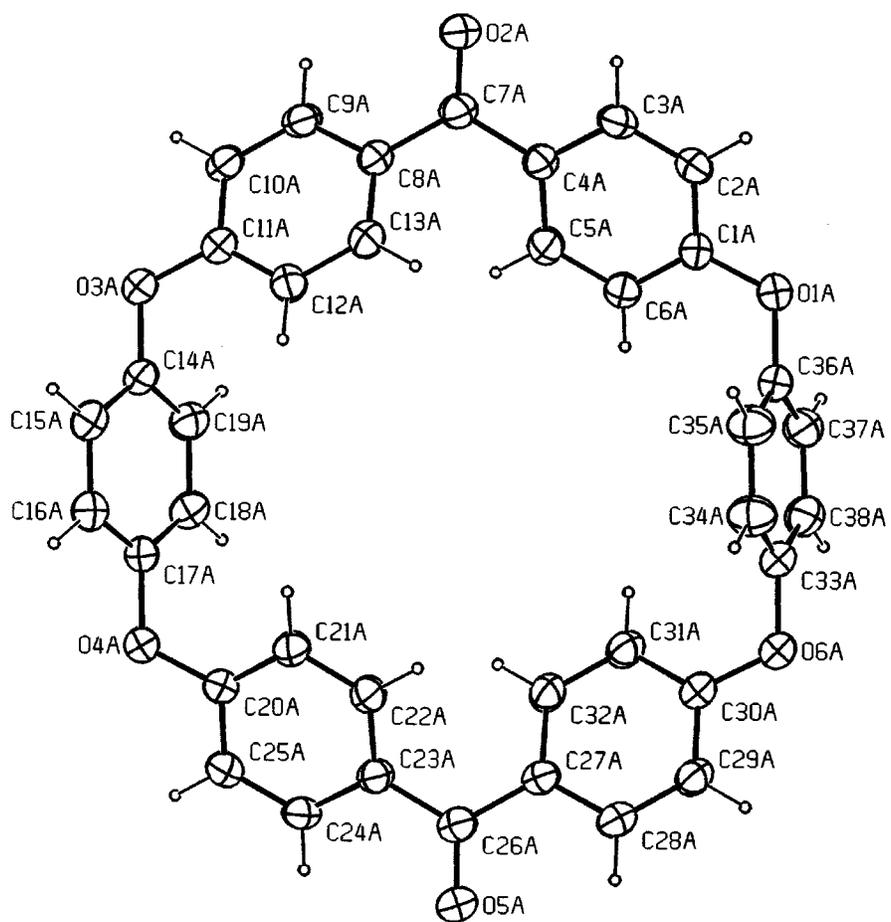


Figure 3.19. Single crystal X-ray structure of cyclic dimer.

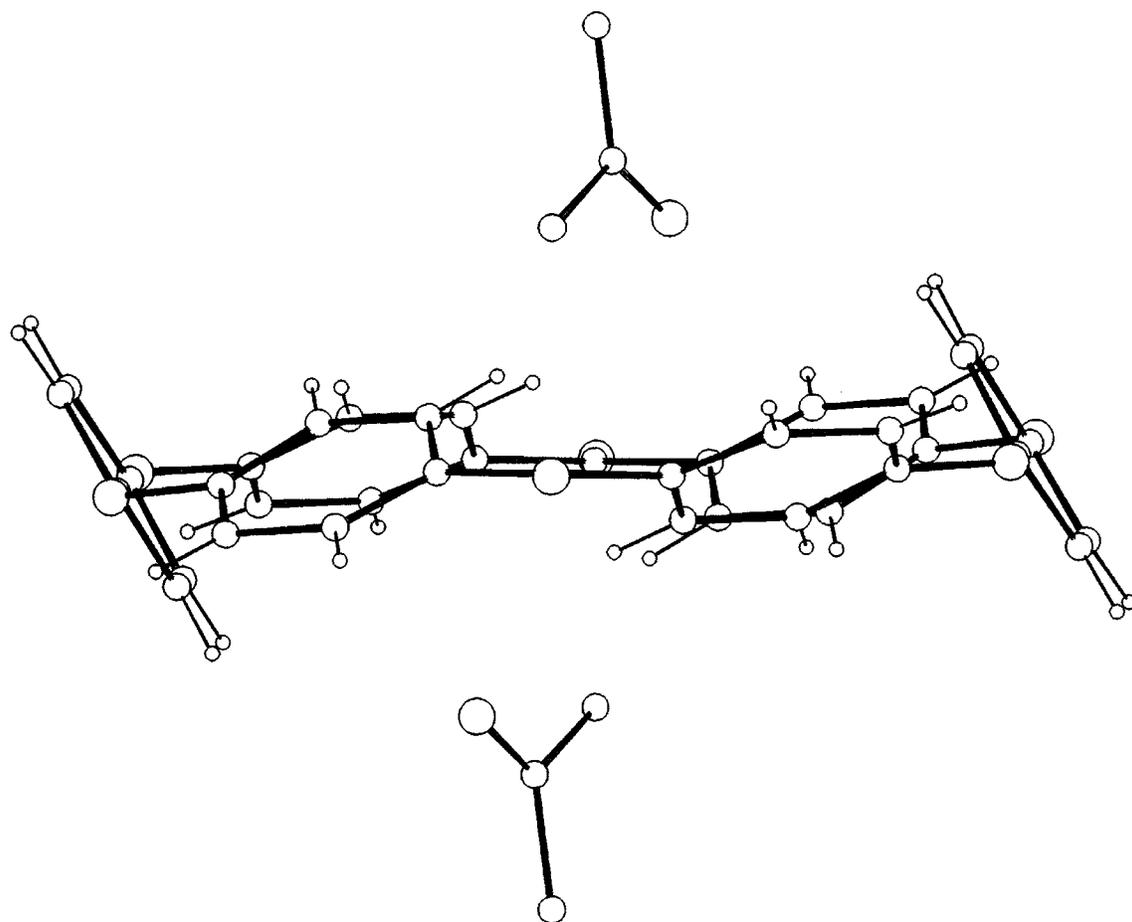


Figure 3.20. Single crystal X-ray structure of cyclic dimer (side view). The small molecules are acetone.

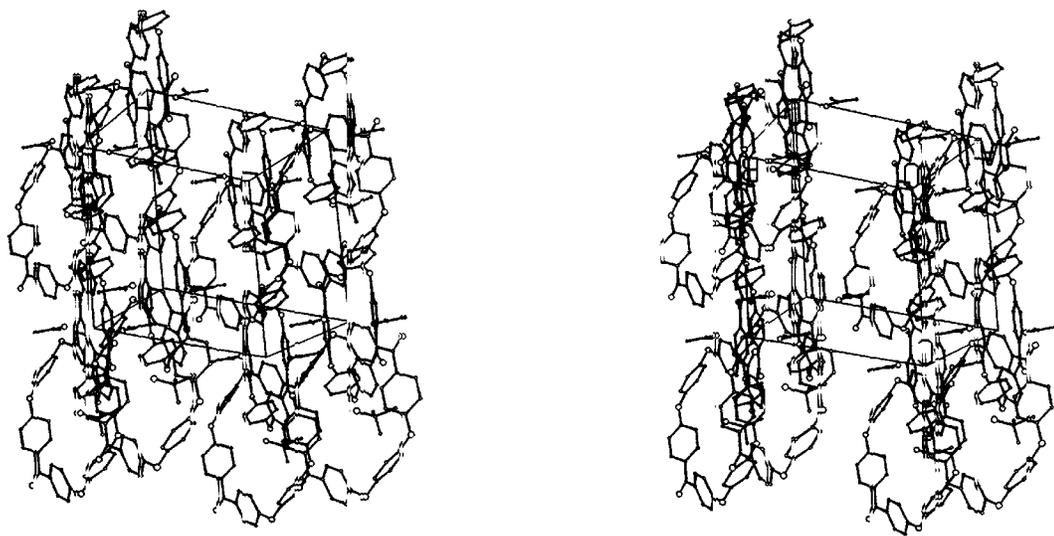
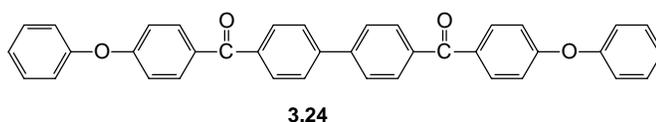
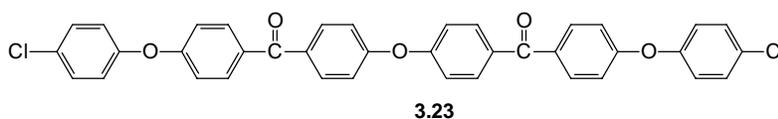


Figure 3.21. Packing diagram of cyclic dimer.

centroid-to-centroid distance between rings C(5A)-C(6A) and C(21A)-C(22A) is 9.96 Å. The corresponding distance between the centroids of ring C(18A)-C(19A) and C(34A)-C(35A) is 10.50 Å. It is interesting to compare the geometric parameters of the aromatic ether ketone macrocycle with the linear model ether ketone compounds **3.23** and **3.24** reported by Colquhoun and coworkers.¹⁶ From Table 3.1, it can be concluded that the bond lengths of the macrocycle are very close to the values determined for the linear compounds. The average C-O-C bridge angle is 116.7 °, which is about 5 ° lower than for the linear molecules. The average C-carbonyl-C angle is 121.2 °, about 2 ° lower than in the linear molecules. The average torsional angle defined by the ether or ketone phenyl group is 26 °, which is also about 5 ° lower than in the linear molecules. These results suggest that the linear PEEK probably has the same bond lengths as the macrocyclic dimer. Thus the data provided here is quite useful to get the true geometric parameters of PEEK molecules in the crystal structure.



[16] Colquhoun, H. M.; O'Mahoney, C. A.; Williams, D. J. *Polymer* **1993**, 34, 218.

Table 3.1. Average bond lengths (Å) of macrocyclic dimer and trimer compared with linear molecules **3.23** and **3.24**

Bond	Linear Molecule 3.23	Linear Molecule 3.24	Cyclic Dimer	Cyclic Trimer
Ar-CO	1.486	1.490	1.487	1.492
Ar-O	1.386	1.388	1.391	1.394
C-C(Ar)	1.384	1.383	1.378	1.383
C=O	1.223	1.223	1.227	1.228

Table 3.2 Bond Angle Comparison

Bond Angle	Cyclic Dimer	Cyclic Trimer
C-O-C	116.7	119.2
C-CO-C	121.2	120.9

The cyclic trimer and hexamer were separated by column chromatography on silica gel with methylene chloride as the eluent. The ^1H NMR spectrum of the cyclic trimer has the same pattern as that of the cyclic dimer (Figure 3.16). However, the proton ortho to the carbonyl group moves downfield, indicating the ring strain has decreased. The ring size was confirmed by the FABMS spectrum, which shows the calculated pseudo molecular ion at $[\text{M}+\text{H}]^+$ peak at 864.2.

On the heating curve of the DSC thermogram of the cyclic trimer (Figure 3.22), there are three sharp endothermic peaks. The peak at 366 °C corresponds to the melting as verified by visual observation in the melting point apparatus. The two other sharp peaks around 278 °C and 317 °C are probably due to crystal-discotic liquid crystal, discotic-nematic and nematic-isotropic

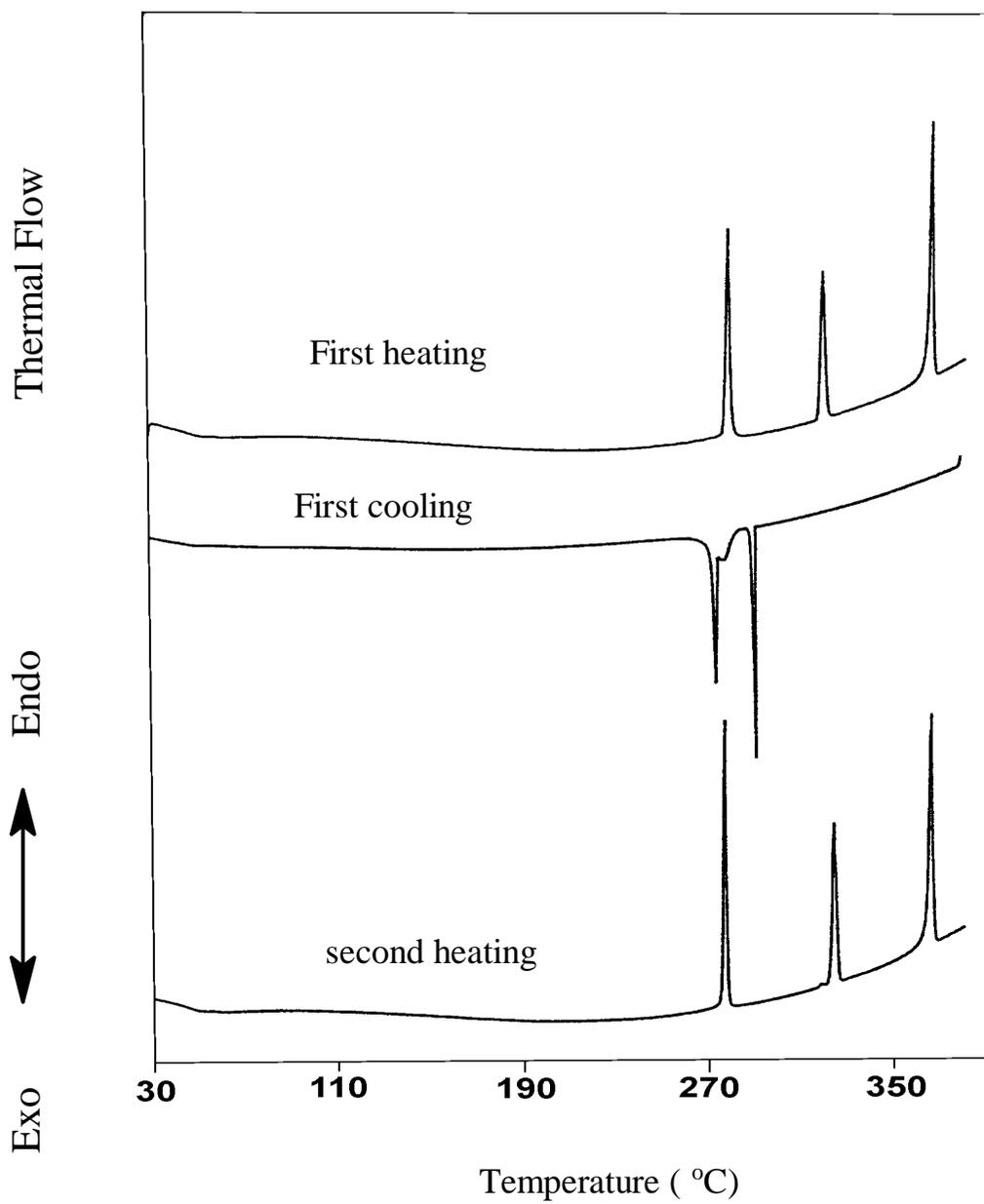


Figure 3.22. DSC thermograms of cyclic trimer.

transitions . On the cooling curve, there are two sharp crystallization peaks at 288 and 272 °C, respectively. These two peaks also show up on the second heating curve at slightly different temperatures.

Single crystals of cyclic trimer were grown from THF solution, while hexane vapors gradually diffused into the solution. The X-ray structure of the macrocycle is shown in Figures 3.23-25. The crystal space group is P-1 with unit cell parameters $a=9.729$, $b=16.7545$, $c=17.5404$ Å; $\alpha=72.745$, $\beta=80.117$ and $\gamma=84.133^\circ$. Detailed X-ray structural data is listed in Appendix C. In contrast to the cyclic dimer, the cyclic trimer adopts a more flexible conformation in approximately the shape of a bowl. The macrocycle adopts a conformation somewhat collapsed towards the center of the molecule. However, the cavity is still quite open. The dimension of the cavity is approximately defined by the distance of the centroid of ring C(47)-C(48) to C(20) (15.07 Å) vs. the distance between the centroid of ring C(33)-C(34) and O(2) (13.43 Å). This is an enormous cavity with high possibility of penetration by linear molecules. The molecule is also somewhat twisted from the side view. All the phenyl groups adopt trans configurations relative to the ether and the carbonyl bridges. Compared with the cyclic dimer, there is not much difference in the bond lengths (Table 3.2). Interestingly, the average ketone bridge angle (C-carbonyl-C) is almost the same for the two cyclic molecules and the linear molecules **3.23** and **3.24** (Table 3.2). The average ether bridge angle (C-O-C) is 2.5 ° higher than that of cyclic dimer. This clearly indicates that the ketone bridge is more rigid

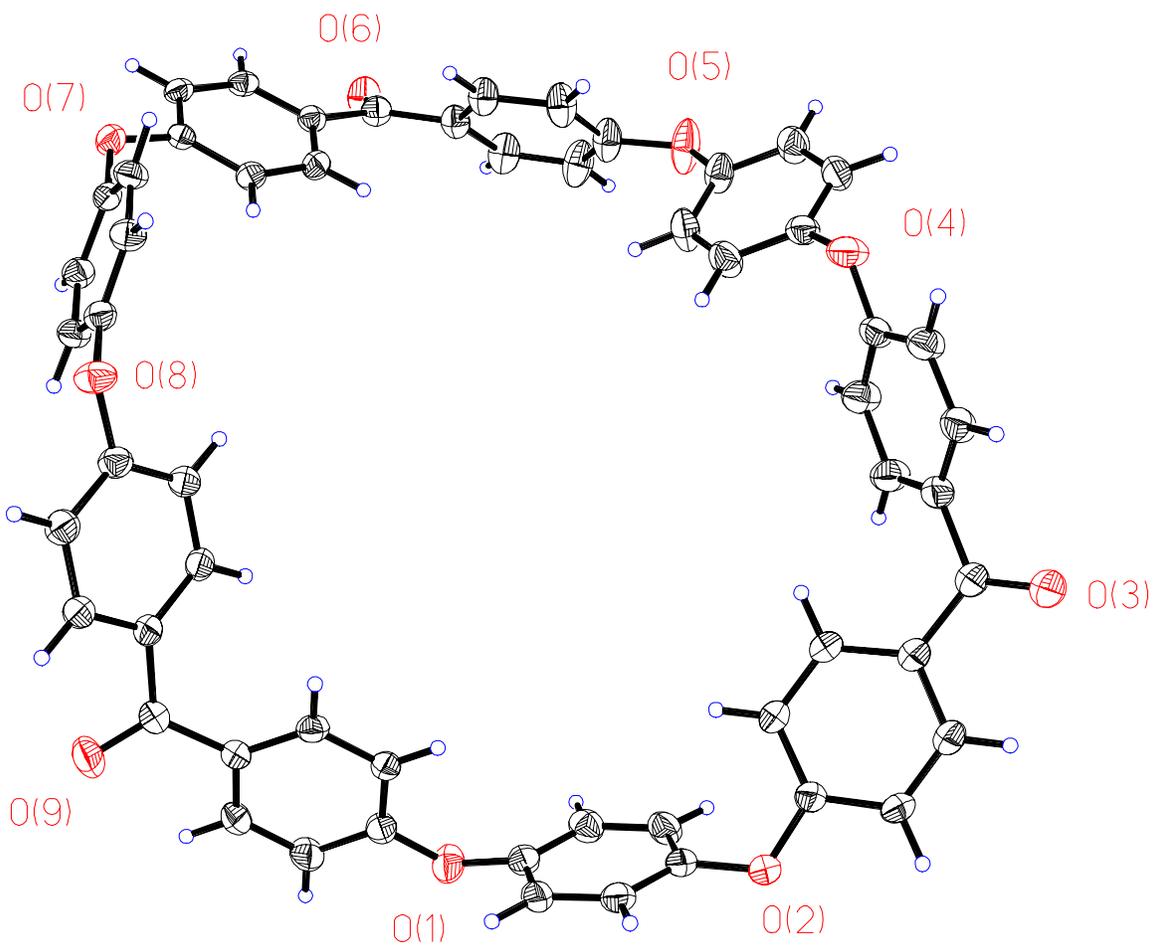


Figure 3.23 Single crystal X-ray structure of cyclic trimer.

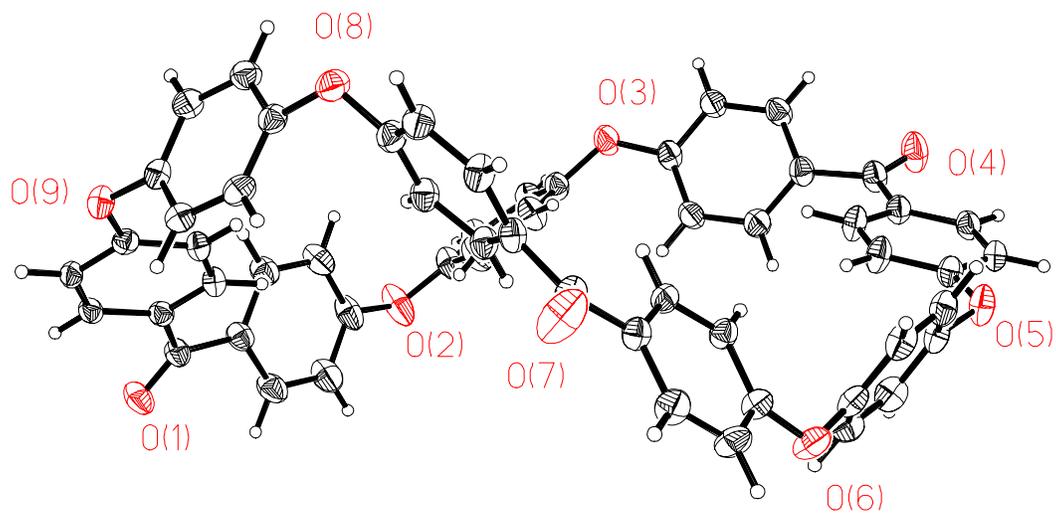


Figure 3.24. Single crystal structure of cyclic trimer (side view)--twist conformation.

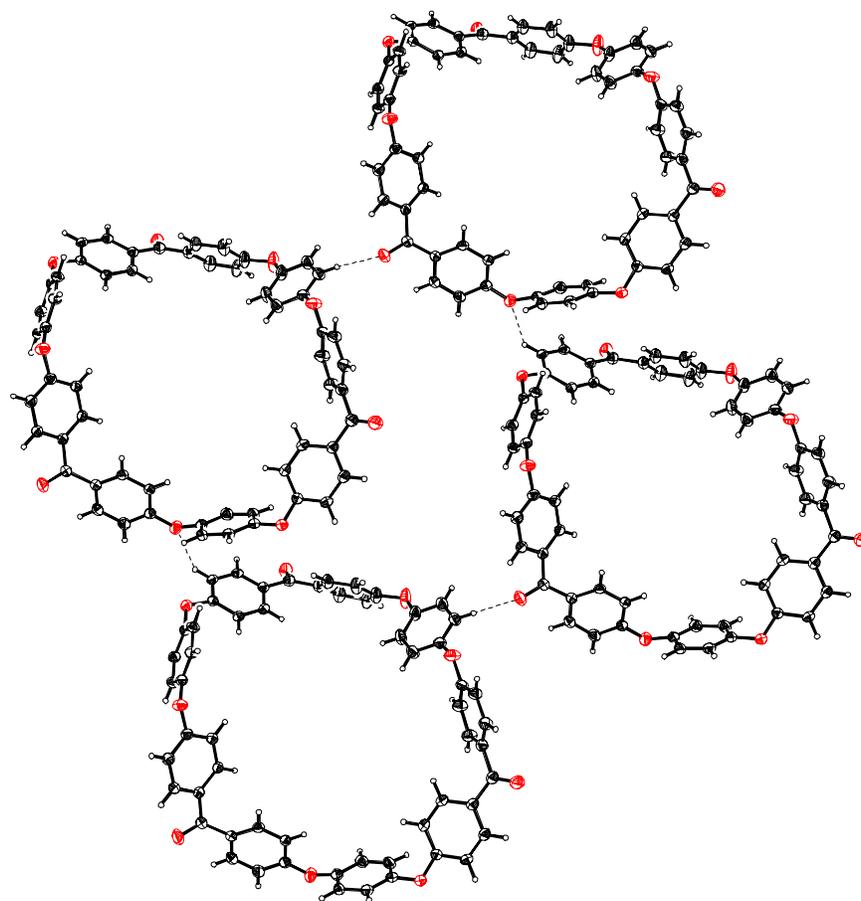


Figure 3.25. Packing diagram of cyclic trimer.

than the ether bridge, which is thus more deformed to adapt to the cyclic structure.

In the crystal packing diagram (Figure 3.25), it can be seen that the macrocycles are organized by hydrogen bonding interactions of the ether oxygen atoms and the phenyl protons. There seems also to be some π interaction through an edge-face configuration.

Similarly, the structure of cyclic tetramer was established by NMR and FABMS. The chemical shift in the proton NMR spectrum is quite different from the other macrocycles but with the same pattern (Figure 3.16). The FABMS shows the pseudo molecular ion peak at $[M+H]^+=1153.6$ (calculated 1153.3, Figure 3.26).

The macrocyclic tetramer has extremely high thermal stability as can be seen from its TGA thermogram (Figure 3.27). It has a 5 % weight loss temperature of 597 °C in nitrogen and 561 °C in air. There is almost no weight loss up to 480 °C. This is of course due to the fully aromatic structure.

DSC thermograms of the cyclic tetramer are shown in Figure 3.28. In the first heating of the virgin sample, there are three melting peaks between 270-350 °C. The highest melting peak is located at 333 °C. There is no detectable transition on the cooling curve. On the second heating curve, T_g is seen at 150 °C, which is followed by crystallization between 210-280 °C. There is only a single melting point at 315 °C, which lowered by 18 °C compared with the virgin sample.

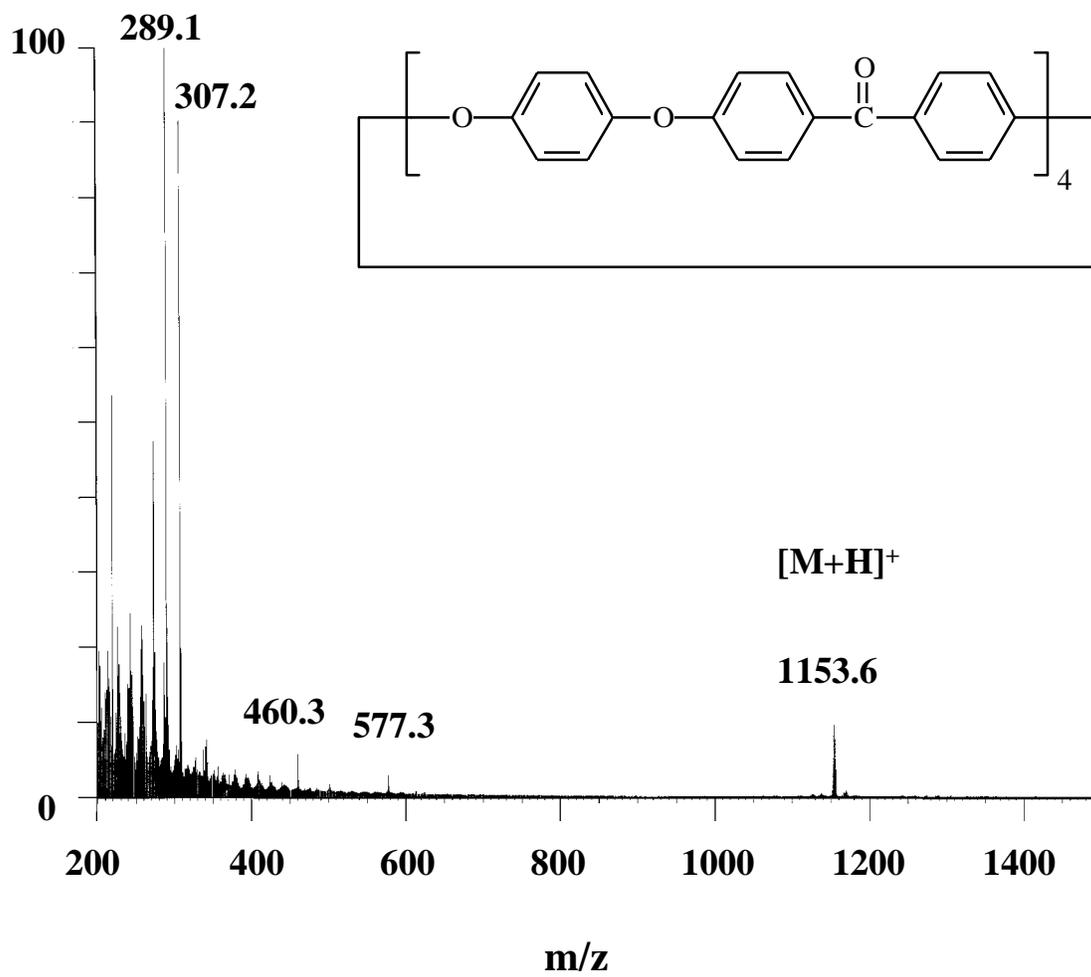


Figure 3.26. FABMS spectrum of cyclic tetramer in 3-NBA matrix.

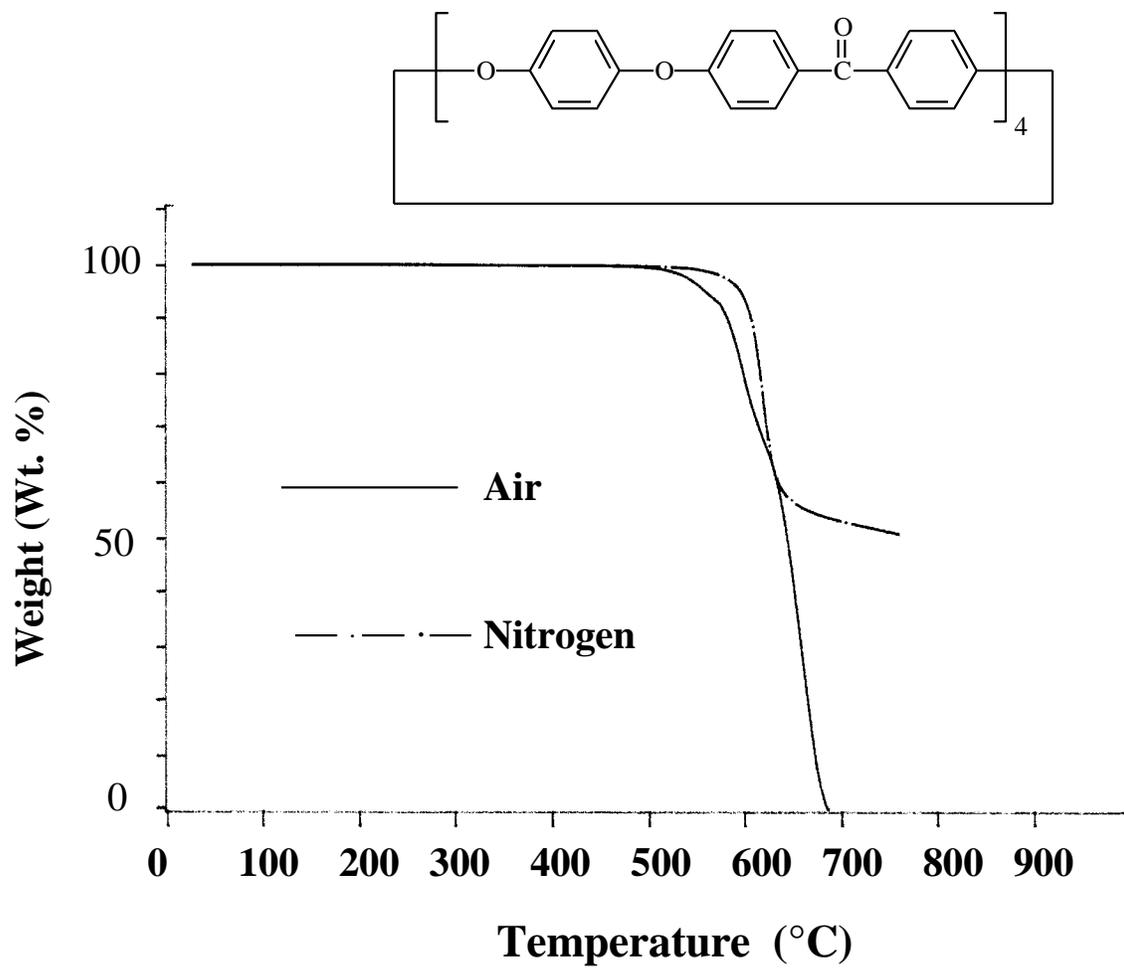


Figure 3.27. TGA thermograms of cyclic tetramer at a heating rate of 10 °C/min.

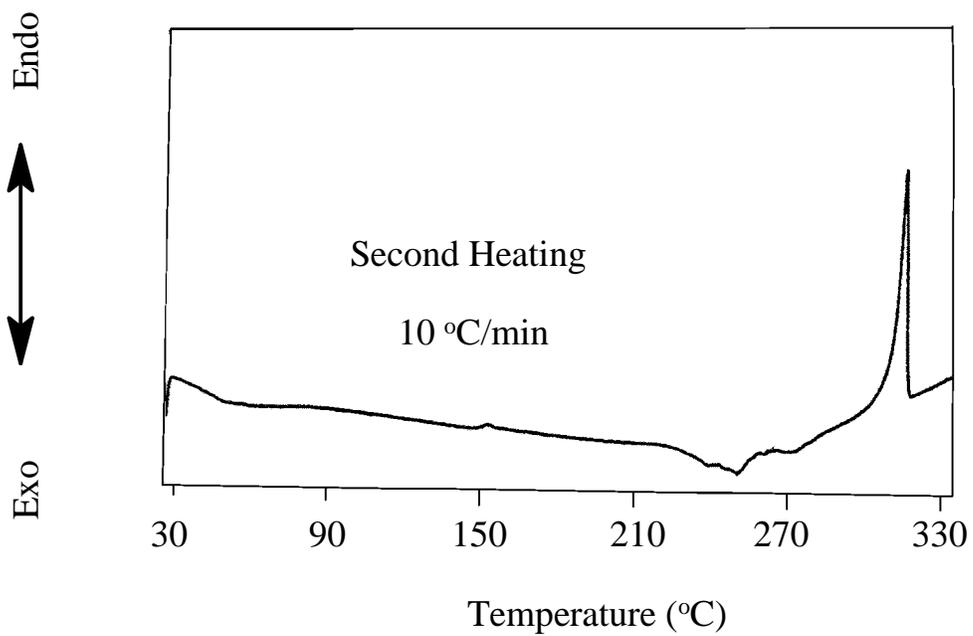
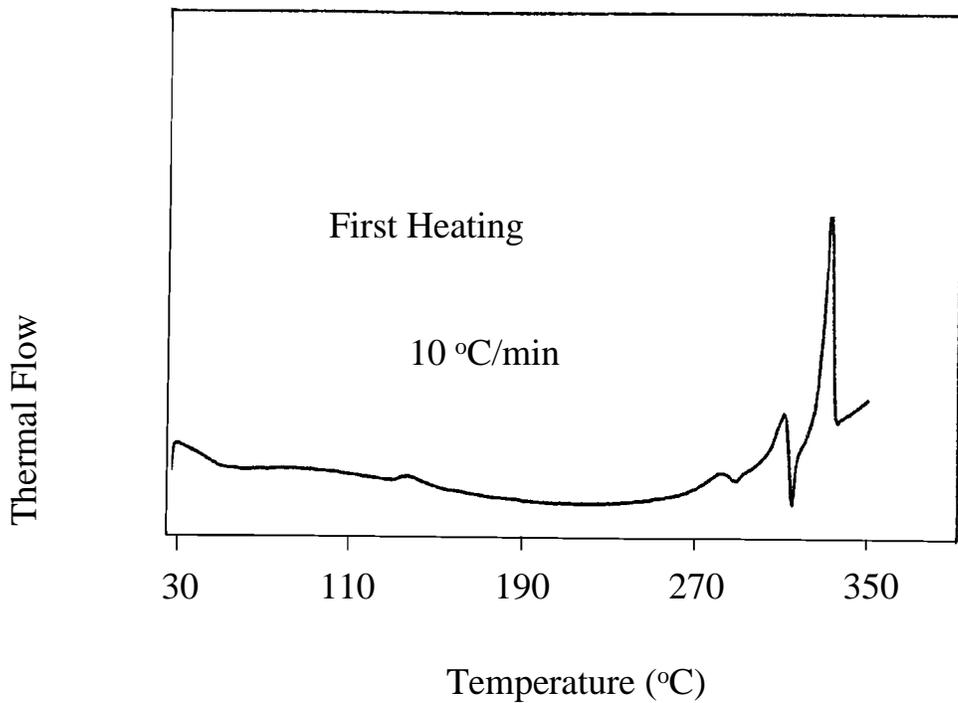


Figure 3.28. DSC thermograms of cyclic tetramer at a heating rate of 10 °C/min.

The structure of cyclic hexamer was confirmed by FABMS and NMR analysis. FABMS shows a pseudo molecular ion peak for $[M+H]^+$ at $m/z=1729.8$. The proton NMR spectrum of the macrocycle is not very much different from the cyclic tetramer in chloroform-d (Figure 3.16). In the first heating curve of the DSC thermograms (Figure 3.29), the macrocycle shows double melting peaks at 304 and 324 °C. On the second heating curve, a T_g is seen at 148 °C, slightly lower than that of cyclic tetramer. Also there is a crystallization peak at 227 °C. The double melting peaks are lowered to 290 and 306 °C. This behavior is similar to that of the cyclic tetramer.

It is well known that for a linear polymer, the melting point increases with an increase molecular weight. To summarize, what we have seen here is that the melting points of the macrocycles decrease with increasing ring size. This is the direct result of an increase in the flexibility, i. e., an entropic effect.

The mixture of cyclic trimer and hexamer shows 5 % weight loss temperature at 543 °C in air and 557 °C in the nitrogen atmosphere.

The rheological properties of the cyclic mixture of trimer and hexamer were studied. Mullins and coworkers found that their cyclic sulfone was not stable in the melt.¹⁷ They attributed this to the unremoved reactive terminal phenoxide group. They had to pass the cyclics through an anion exchange column to remove the terminal group. Hay's group found that the cyclic mixture

[17] Mullins, M. J.; Woo, E. P.; Murry, D. J.; Bishop, M. T. *Chemtech* **1993**, Aug. 25.

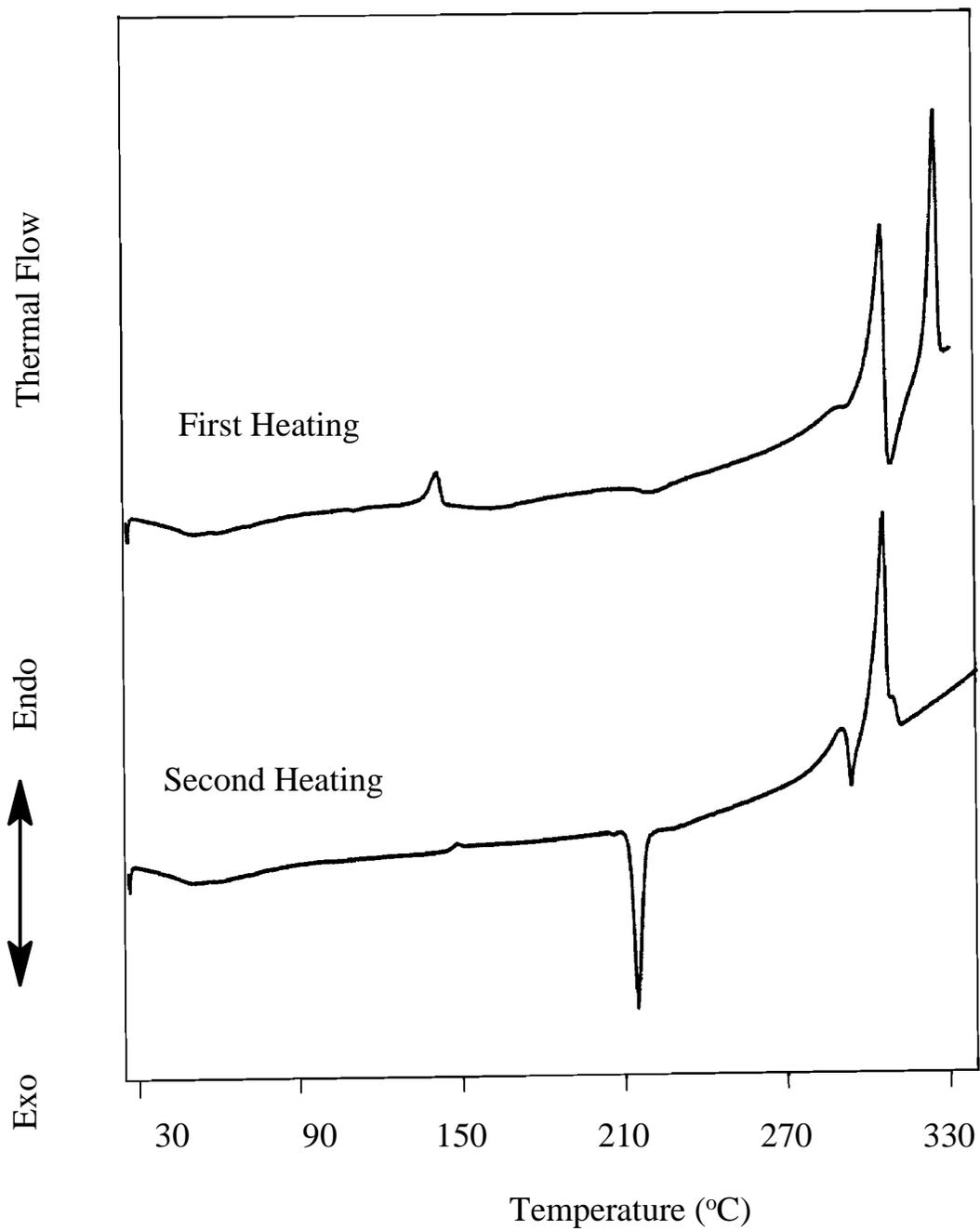


Figure 3.29. DSC thermograms of cyclic hexamer at a heating rate of 10 °C/min.

was also unstable due to residual potassium carbonate, which can initiate the ring-opening polymerization of the cyclics. Our cyclic product showed extremely high melt stability. The cyclic mixture was under constant shear at a rate of 50 rad/s at 350 °C for about 2 hours and there was almost no change of viscosity (Figure 3.30). This high melt stability is a direct result of the high purity of the macrocycle without contamination from linear oligomers. Also from Figure 3.30, the low viscosity nature of the macrocycle is evident. The macrocycle has a melt viscosity of only 0.12 Pa.s, while the commercial linear PEEK has a melt viscosity of several thousand Pa.s. Thus, the macrocyclic mixture has a viscosity about four orders of magnitude lower than the commercial polymers. Quiet surprisingly, the cyclic mixture is a non-Newtonian fluid. The viscosity decreases with increasing shear rate, similar to high molecular weight linear polymers (shear thinning). Linear high molecular weight polymers are typically non-Newtonian because of chain entanglement. Lower molecular weight polymers, because of lack of chain entanglement, behave as Newtonian fluids. Since the cyclic has an average size less than four repeat units, there should not be any entanglement. Thus this non-Newtonian behavior is probably related to the cyclic structure, which induces order in the melt.

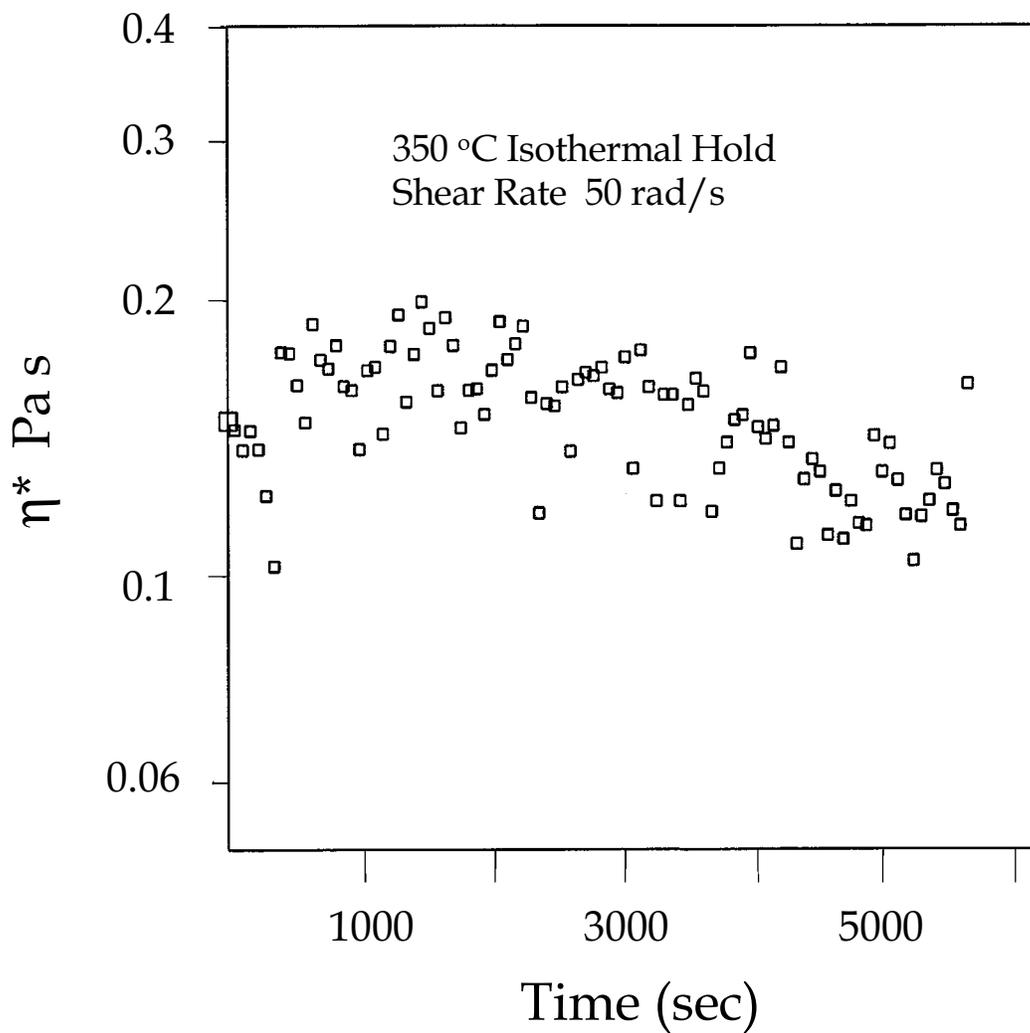
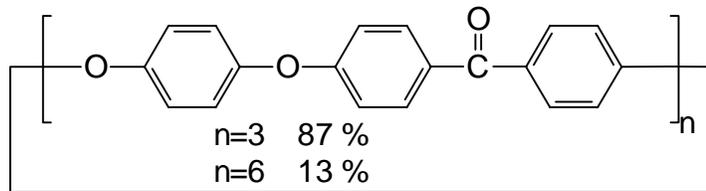


Figure 3.30. Melt viscosity stability of a cyclic mixture at 350 °C under 50 rad/s shear.

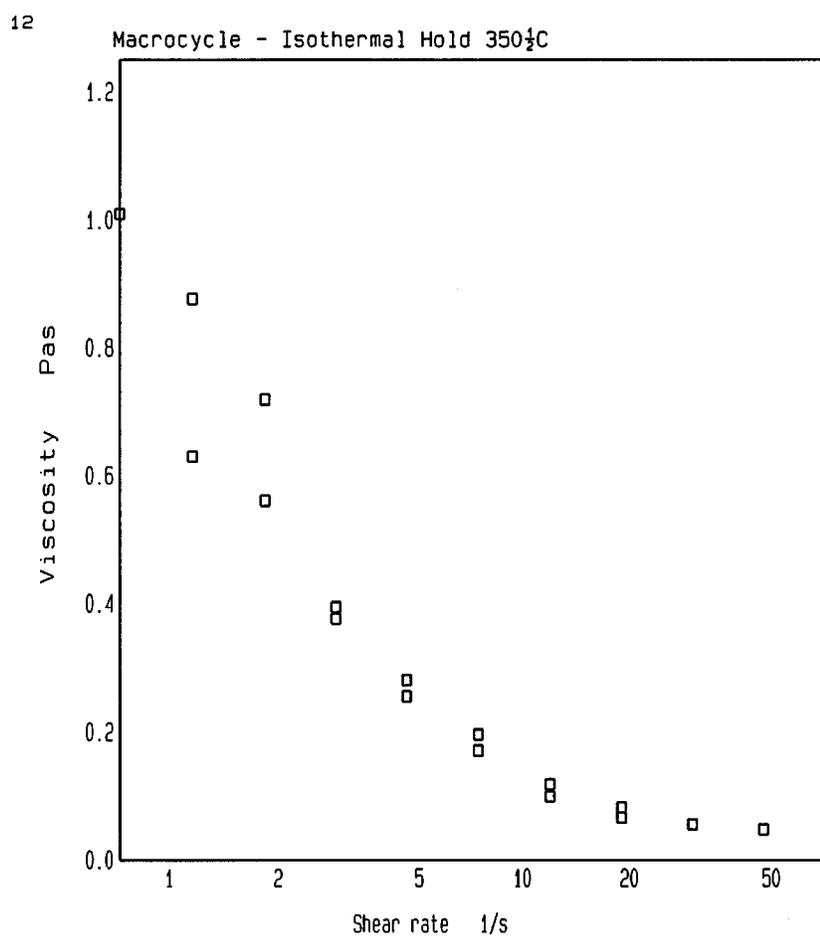
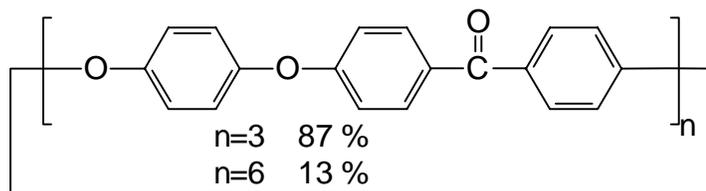


Figure 3.31. Dependence of viscosity of a cyclic mixture on shear rate at 350 °C.

3.5 Conclusions

1. Macrocyclic monomers of poly(ether ether ketone) with up to six repeating units were synthesized. Simple extraction afforded cyclic mixtures without contamination from linear oligomers. The pure, single-size macrocycles were isolated by recrystallization or column chromatography and fully characterized.
2. This study further supports the previous conclusion that the cyclic distribution is predominantly kinetically controlled. Use of short starting materials results in predominantly cyclic dimer and high melting point cyclic mixtures. We are able to bring down the melting point of the cyclic monomer to reasonably low range by synthesizing large sized macrocycles.
3. Single crystal X-ray structural results for cyclic dimer and trimer have shown that a macrocycle gains more flexibility with increasing ring size. The ketone bridge is more rigid than the ether bridge. The bond lengths of the macrocycles are not very much different from the linear model compounds. This suggests that the linear poly(ether ether ketone) and the cyclic oligomers have the same bond lengths.
4. The macrocycles show thermal stability comparable to linear PEEK. In contrast to linear polymers, the melting points of the cyclics decrease with increasing ring size or molecular weight.
5. Rheological studies show that the melt of the cyclic mixture is non-Newtonian. The melt viscosity is about 4 orders of magnitude lower than that of the corresponding high molecular weight linear polymers.

3.6 Experimental Part

Materials. All the starting materials were used as provided. 4,4'-Difluorobenzophenone, 4,4'-dichlorobenzophenone, hydroquinone, phenol, 4-fluorobenzoyl chloride, potassium and benzyl bromide were received from Aldrich. Dimethylacetamide and toluene were provided by Fisher.

Measurements. A Harvard Model 22 syringe pump or a Sage Instruments Model 355 syringe pump was used to control the addition rate in the cyclization reaction. Melting points were determined on a Haake-Buchler capillary melting point apparatus and were corrected unless otherwise specified. NMR spectra were recorded on a Varian Unity 400 MHz spectrometer. Infrared spectra (KBr pellets) were taken on a Nicolet MX-1 FTIR spectrometer. TGA was performed on a Perkin-Elmer Model TGA-7 under nitrogen and air at a heating rate of 10 °C/min. The FABMS spectra were obtained from Midwest Center for Mass Spectrometry at the University of Nebraska-Lincoln. The matrix for FABMS experiment was 3-nitrobenzyl alcohol. Reverse-phase HPLC analyses were performed on an ISCO dual pump HPLC system comprising two Model 2350 pumps and a UV/Vis detector set at 275 nm. Tetrahydrofuran/water linear gradients were used for elution on a Novapak C-18 reverse-phase column at a flow rate of 1.5 mL/min. The gradient used for analysis was as follows: solvent A. THF; solvent B, 65:35 (v/v)THF/water, the amount of B was changed from 100 % to 20 % over a period of 20 minutes. The system was interfaced with the

ISCO ChemResearch Chromatographic Data Management/System for data analyses.

Rheological Measurements

Rheological experiments were carried out on a Bohlin VOR rheometer with a 25 mm diameter parallel plate fixture. A Bohlin HTC using nitrogen as the heating gas was used for temperature control. About 0.5 g of sample compressed in a cake was used in the experiments. The samples were placed between two plates. All the measurements were made under nitrogen atmosphere.

X-ray Structure Determination

Single crystals of macrocyclic dimer were obtained from dilute acetone solution by slow evaporation of the solvent. A colorless crystal of dimensions 0.2x0.25x0.33 mm, sealed in a capillary, was used for data collection on an Enraf-Nonius CAD4 diffractometer equipped with $\text{CuK}\alpha$ radiation ($\lambda=1.54184 \text{ \AA}$), and a graphite monochromator.¹⁸ Crystal data are: $\text{C}_{38}\text{H}_{24}\text{O}_6 \cdot 4/3 \text{ C}_3\text{H}_6\text{O}$. $M_p=651.1$, triclinic space group P-1, $a=12.4803(7)$, $b=14.431(2)$, $c=14.6287(9)\text{ \AA}$, $\alpha=99.348(7)$, $\beta=90.173(5)$, $\gamma=94.830(7)^\circ$, $V=2590.1(8)\text{ \AA}^3$, $Z=3$, $d_c=1.258 \text{ g cm}^{-3}$, $T=22 \text{ }^\circ\text{C}$. Intensity data were measured by w -2 θ scans of variable rate. A

[18] The X-ray structure was kindly provided by Dr. Frank Fronczek at Louisiana State University, Baton Rouge, Louisiana 70803.

hemisphere of data was collected within the limits $2 < \theta < 75^\circ$. Data reduction included corrections for background, Lorentz, polarization, decay, and absorption effects. Absorption corrections ($\mu = 6.6 \text{ cm}^{-1}$) were based on ψ scans, with minimum relative transmission coefficient 92.8%. Intensity decay amounted to 21.5%, and a linear correction was applied. Of 10,456 unique data, 5456 had $I > 3\sigma(I)$ and were used in the refinement.

The structure was solved by direct methods using SHELX,¹⁹ and refined by full-matrix least squares, using the Enraf-Nonius MolEN programs.²⁰ Nonhydrogen atoms were treated anisotropically. Hydrogen atoms were placed in calculated positions, except for those of the acetone molecules, which could not be located because of the disorder and high thermal parameters. Convergence was achieved with $R = 0.058$ and $R_w = 0.064$, and maximum residual density $0.55 \text{ e}\text{\AA}^{-3}$.

Single crystals of cyclic trimer were grown from THF solution while hexane vapors gradually diffused into the solution over about one week. A colorless flat crystal with a size about $0.40 \times 0.40 \times 0.20 \text{ mm}$ was used for X-ray analysis. The X-ray structure determination was performed on a CCD-detector equipped Siemens P4 diffractometer with molybdenum-target tube.²¹ Of 9787 data

[19] Sheldrick, G. M. *Acta Cryst.* 1990, A46, 467-473.

[20] Fair, F. C. 'MolEN. An Interactive System for Crystal Structure Analysis', Enraf-Nonius, Delft, The Netherlands, 1990.

[21] The X-ray structure was kindly provided by Louise Liable-Sands of Dr. Arnold L. Rheingold's group at University of Delaware, Newark, Delaware 19176.

collected, there were 7313 independent reflections. The structure was solved by SHELTXL-Pus software and refined by full-matrix least-square on F^2 . Final R= 0.0568.

Synthesis of Monobenzyl Ether of Hydroquinone (3.3)

To a 1000 mL three neck-round flask were added 500 mL 100 % ethanol and 2 drops of 10% HCl. The flask were purged thoroughly with nitrogen before the addition of hydroquinone (15.416 g, 0.14 mol) and KOH (16.50 g, 0.28 mol). Benzyl bromide (16.65 mL, 0.14 mol) dissolved in 30 mL ethanol was added dropwise while the system was under reflux and magnetic stirring. The reaction time was three hours. As the system was cooled down the dibenzyl ether of hydroquinone precipitated out. 5 % HCl in ethanol was added to neutralize the solution to pH=7. The white precipitate was filtered. Ethanol was removed from the filtrate and the slightly brown solid obtained was washed with deionized water to get rid of hydroquinone, which is soluble in water. The crude product was recrystallized in 30 % hexane-ethyl acetate to give a pure colorless product. Yield: 13.4 g (48 %); mp 120.4-122.0 °C (lit.²² mp 120-122 °C) ; ^1H NMR (270 MHz, CDCl_3): δ =7.32-7.45 (m, 5H), 6.87 (d, 2H), 6.76 (d, 2H), 5.01 (s, 2H); FTIR(KBr): 3409 (OH), 3037 (Ar-H), 2904, 2864, 1603, 1501, 1238, 1018, 819, 773, 739, 700.

[22] Leznoff, D. *Can. J. Chem.* **1977**, 55, 3351.

Synthesis of 4,4'-Bis(4-benzyloxyphenoxy)benzophenone (3.6)

To a 1000 mL three-neck round bottom flask were added the monobenzyl ether of hydroquinone (8.000 g, 40 mmol), potassium carbonate (3.04 g, 22 mmol), 200 mL DMAc and 100 mL toluene. The flask was equipped with a Dean-Stark trap and mechanical stirrer. The system was under nitrogen protection. The azeotropic distillation took three hours to remove all water. Toluene was distilled off and the system was cooled down to room temperature and then 4,4'-difluorobenzophenone (4.362 g, 20 mmol) was added. The reaction was kept at reflux for 24 hours. Upon cooling, the product precipitated from the solution. DMAc was removed under vacuum and the solid obtained was washed with water and ethanol. The crude product was crystallized in DMAc to give a pure compound. Yield 5.9 g (51 %); mp 229.2-232.0 °C; ¹H NMR (270 MHz, CDCl₃): δ=7.75 (d, 4H), 7.34-7.46 (m, 10H), 7.01 (s, 4H), 6.97 (d, 4H), 5.07 (s, 4H); FTIR(KBr): 3062, 2910, 2850, 1644 (carbonyl), 1601, 1506, 1244, 1164, 1017, 842, 735, 692.

Syntheses of 4,4'-Bis(4-hydroxyphenoxy)benzophenone (3.7) and 4,4'-Bis(4-(4-(4-hydroxyphenoxy)benzoyl)phenoxy)benzene (3.8)

To a 2L round bottom flask equipped with a Dean Stark trap, mechanical stirring, and nitrogen inlet and outlet were added 500 mL DMAc, 260 mL toluene, hydroquinone (66.0 g, 600 mmol), and K₂CO₃ (91 g, 660 mmol). The solution was kept at reflux over 4 hours to remove water by azeotropic distillation. The system was cooled down to room temperature and 4,4'-difluorobenzophenone

(6.5458 g, 30.0 mmol) was added. The solution was kept at reflux for 24 hours and then toluene was removed. The reaction was refluxed for another 5 hours, cooled, neutralized by 10% HCl to pH=7 and then poured into 2500 mL water to precipitate the product. The precipitate was filtered and washed with water and dried. The solid was extracted with acetone. The acetone solution was loaded onto a silica gel column and eluted with 1.5:1 hexanes/ethyl acetate. Yield of **3.7**: 10.54 g (88 %); mp 228.1-230.8 °C (lit.²³ mp 214 °C); ¹H NMR (400 MHz, acetone-d₆): δ=7.78 (d, J=8.8 Hz, 4H), 7.01 (d, J=8.8 Hz, 4H), 7.00 (d, J=8.8 Hz, 4H), 6.91 (d, J=8.8 Hz, 4H); CIMS: 399.0, [M+H]⁺, calculated: 399.1. **3.8** was extracted from the acetone insoluble part with DMAc. Yield of **3.8**: 1.60g (7%), mp 255 °C (determined by DSC, heating rate 10 °C/min); ¹H NMR (400 MHz, DMSO-d₆): δ=9.52 (s, 2H, OH), 7.77 (d, J=8.8 Hz, 4H), 7.74 (d, J=8.8 Hz, 4H), 7.25 (s, 4H), 7.12 (d, J=8.8 Hz, 4H), 6.99 (d, J=8.8 Hz, 8H), 6.83 (d, J=8.8 Hz, 4H); FABMS: 687.0, [M+H]⁺; calculated: 687.2. Compound **3.7** was also synthesized from 4,4'-dichlorobenzophenone using similar procedures and the final product was isolated by extraction with acetone and purified by recrystallization in methanol.

Synthesis of 4-Phenoxyphenol (**3.9**)

A 250 mL round bottom three-neck flask equipped with a condenser, a Dean-Stark trap, N₂ inlet and outlet and a magnetic stirrer bar was charged with

[23] Dilthey, J. P. *J. Prakt. Chem.* **1933**, 49, 69.

phenol (40 g, 0.43 mol), KOH (7.2 g, 0.13 mol) and 100 mL toluene. Water was removed by azeotropic distillation over about 4 hours. After the toluene was removed, copper powder (0.3 g, 4.7 mmol) and 4-chlorophenol (10.9 g, 85 mmol) were added. The color became deep purple within about 1 hour. The reaction mixture was kept at reflux (210 °C) for 12 hours and poured into water and neutralized by 10 % aqueous HCl. The product was extracted with chloroform. Chloroform was removed on a rotatory evaporator and excess phenol was removed by aspirator at about 100 °C. The remaining black residue was vacuum distilled at 3 mm Hg (150-220 °C). The pink distillate was recrystallized in toluene to get pure 4-phenoxyphenol. Yield: 2.7 g (17 %); m p 85-85.8 °C (lit.²⁴ mp 83-85 °C). ¹H NMR (400 MHz, CDCl₃): δ=7.30 (t, J=8.8 Hz, 2H), 7.04 (t, J=8.8 Hz, 1H), 6.93 (m, 4H), 6.81 (d, J=8.8 Hz, 2H), 4.80 (s, 1H).

Synthesis of p-Phenoxyphenyl acetate (3.10)

To a 100 mL one-neck round bottom flask with a magnetic stirrer bar and condenser were added 30 mL methylene chloride, 4-phenoxyphenol (2.48 g, 13.3 mmol) and acetic anhydride (4.0 g, 40 mmol) and 1 mL pyridine. The reaction was kept at reflux overnight. Solvent and excess pyridine were removed on a rotatory evaporator to get a liquid, which was redissolved in methylene chloride. The solution was repeatedly washed with deionized water. Methylene

[24] Tashiro M. *Synthesis*, **1978**, 399.

chloride was removed on a rotatory evaporator. The product was a liquid.²⁵

Yield 2.79 g (92 %); ¹H NMR (400 MHz, CDCl₃): δ=7.34 (t, J=8.8 Hz, 2H), 7.10 (t, J=8.8 Hz, 1H), 6.98-7.07 (m, 4H), 2.29 (s, 3H).

Synthesis of 4-(p-Acetoxyphenoxy)-4'-fluoro-benzophenone (3.12)

To a 250 mL round bottom flask with a condenser and a magnetic stirrer bar were added 100 mL methylene chloride (distilled over P₂O₅), dried **3.10** (3.04g, 13 mmol), AlCl₃ (3.92g, 29 mmol) and 4-fluorobenzoyl chloride (2.11 g, 13.3 mmol). The reaction mixture became dark brown upon addition of 4-fluorobenzoyl chloride and HCl was generated immediately. The reaction was kept at reflux for 4 hours. Solvent was removed by a rotatory evaporator and the solid obtained was quenched with 200 mL 10 % HCl and thoroughly washed with deionized water. Pure product was obtained by recrystallization in methanol. Yield 3.03 g (65 %); mp 112.2-114.0 °C; ¹H NMR (400 MHz, CDCl₃): δ=7.82 (2d, 2H, J=8.8 Hz, J=8.8 Hz), 7.79 (d, 2H, J=8.8 Hz), 7.16 (t, 2H, J=8.8 Hz), 7.08-7.14(m, 4H), 2.30 (s, 3H).

Synthesis of 4-(p-Hydroxyphenoxy)-4'-fluorobenzophenone (3.12)

To a 250 mL round bottom one-neck flask were added **16** (2.46g, 7 mmol), 100 mL absolute ethanol, KOH (5.0g, 89 mmol) and 15 mL water. The reaction mixture was stirred at room temperature for 2 hours and no reaction was effected as detected by TLC. The reaction was kept at reflux for two hours and

[25] Yager, G. W.; Shissel, D. N. *Synthesis*, **1991**, 63.

reaction was completed. Water was removed on a rotatory evaporator to get a solid, which was washed with water. The crude product was decolorized with charcoal in ethanol and pure product was obtained by recrystallization in ethanol. Yield 1.297 g (60 %); mp 100.7-102.0 °C; ¹H NMR (400 MHz, CDCl₃): δ=7.81 (2d, 2H, J=8.8 Hz, J=8.8 Hz), 7.77 (d, 2H, J=8.8 Hz), 7.15 (t, 2H, J=8.8 Hz), 7.00 (d, 2H, J=8.8 Hz), 6.98 (d, 2H, J=8.8 Hz), 5.00 (s, 1H).

Synthesis of 4,4'-Bis(p-phenoxyphenoxy)benzophenone (3.14)

To a 100 mL one-neck round bottom flask equipped with a magnetic stirrer bar, a Dean-Stark trap, a condenser and N₂ inlet and outlet were added 50 mL DMAc and 30 mL toluene. The system was refluxed for three hours to remove water. Then 4-phenoxyphenol (5.000 g, 2.7 mmol) and potassium carbonate (2.227 g, 1.6 mmol) were added and the reaction was further dehydrated for two hours before 4,4'-difluorobenzophenone (2.9295 g, 2.7 mmol) was added. The reaction continued overnight. Then toluene was removed and the reflux period was extended two more hours. The product was precipitated in 500 mL water, washed with water and recrystallized in toluene. Yield: 7.3 g (93 %); mp 199.3-200.3 °C (lit.²⁶ mp 198.3-199.3 °C) ; ¹H NMR (400 MHz, CDCl₃): δ=7.80 (d, J=8.8 Hz, 4H), 7.36 (t, J=8.8 Hz, 4H), 7.12 (t, J=8.8 Hz, 2H), 7.0-7.08 (m, 8H).

[26] Jonas, A.; Legras, R. *Macromolecules* **1993**, 26, 526.

Synthesis of 4,4'-Bis(p-(p-(p-fluorobenzoyl)phenoxy)phenoxy)benzophenone (3.15)

To a 250 mL round bottom flask with a magnetic stirrer bar and a condenser capped with mineral oil seal were added 4-fluorobenzoyl chloride (0.9978 g, 6.3 mmol), 30 mL dried methylene chloride and aluminum chloride (1.441 g, 10.8 mmol). Compound **3.14** dissolved in 70 mL methylene chloride was added dropwise. The reaction was under reflux for 24 hours, during which the product precipitated out. The reaction was quenched with 20 mL concentrated HCl. The methylene chloride was removed on a rotatory evaporator. The solid product was washed with water followed by acetone and was recrystallized in DMAc. Yield: 2.30 g (96 %); mp 294 °C (DSC, 10 °C/min) (lit. ²⁶ mp 289.7-290.3 °C); ¹H NMR (400 MHz, 100 °C, d₆-DMSO): δ=7.74-7.86 (m, 12H), 7.33 (t, J=8 Hz, 4H), 7.22 (s, 8H), 7.14 (d, 8 Hz, 8H).

Typical Procedure for Synthesis of Macrocyclic Mixtures by Syringe Pump Technique

To a 1L round bottom flask equipped with a mechanical stirrer, nitrogen inlet and outlet, Dean-stark trap and a condenser were added 260 mL toluene and 500 mL DMAc. The solvent was refluxed for three hours to remove water from the system. The temperature was increased to 135 °C by distillation of some toluene. The system was cooled to room temperature and potassium carbonate (1.6586 g, 12 mmol) was added. A solution of hydroquinone (1.100 g, 10 mmol) and 4,4'-difluorobenzophenone (2.182 g, 10 mmol) in 30 mL DMAc taken from

the flask was injected into the flask at a rate of 0.8 mL /hour with a syringe pump while the system was under reflux. The total reaction time was 64 hours. The solution was filtered to remove the insoluble salt and linear PEEK. Then solvent was removed on a rotatory evaporator to get the macrocyclic mixture. The mixture was thoroughly washed with water and dried in a vacuum oven at 100 °C overnight. Yield: 1.80 g (62 %), mp 402 °C (DSC, 10 °C/min).

Synthesis of Cyclo-tetra(oxy-1,4-phenylene-oxy-1,4-phenylene-carbonyl-1,4-phenylene) (3.21) (Scheme 3.11)

To a 1L round bottom flask equipped with a Dean-Stark trap, a magnetic stirrer bar, nitrogen inlet and outlet were charged with 500 mL DMAc and 260 mL toluene. The system was azeotropically refluxed for four hours before potassium carbonate (0.2500 g, 0.364 mmol) was added. Then four batches of **3.8** (0.2500 g, 0.364 mmol) and **3.13** (0.1840 g, 0.364 mmol) were added over a period of 36 hours. Total reaction time was 65 hours. Salts were filtered and solvents were removed on a rotatory evaporator. The solid obtained was washed with water, dried and exhaustively extracted with chloroform to get the cyclic product. Yield: 1.10 g (66 %). Pure cyclic tetramer was obtained by recrystallization in THF. mp 333 °C (DSC, 10 °C/min); ¹H NMR (400 MHz, CDCl₃): δ=7.81 (d, J=8.8 Hz, 16 H), 7.13 (s, 16 H), 7.04 (d, J=8.8 Hz, 16H); ¹³C NMR (100 MHz, CDCl₃): δ=194.09, 161.51, 152.09, 132.31, 132.27, 132.27, 131.76, 116.94.

Chapter 4

Synthesis and Characterization of Comacrocycles

4.1 Introduction

In previous work, a number of cyclic poly(arylene ether) ketones have been successfully synthesized. These studies as well as literature work have shown that in many cases the melting points of the cyclic mixtures are too high for practical ring-opening polymerization.¹⁻³ The major reason for the high melting points is the presence of a large amount of small sized, highly rigid and symmetric macrocycles, which are formed more favorably during the cyclization process. One approach to reduce the melting point is to control the size distribution of a cyclic mixture by increasing the amount of large sized macrocycles as has been demonstrated in Chapter 2. This is based upon the fact that the melting point of a cyclic oligomer decreases with increasing ring size or molecular weight as has been discussed in Chapter 3.

[1] Chan, K. P.; Wang Y. F.; Hay, A. S.; X. L. Hronowski; Cotter, R. J. *Macromolecules* **1995**, 28, 6705

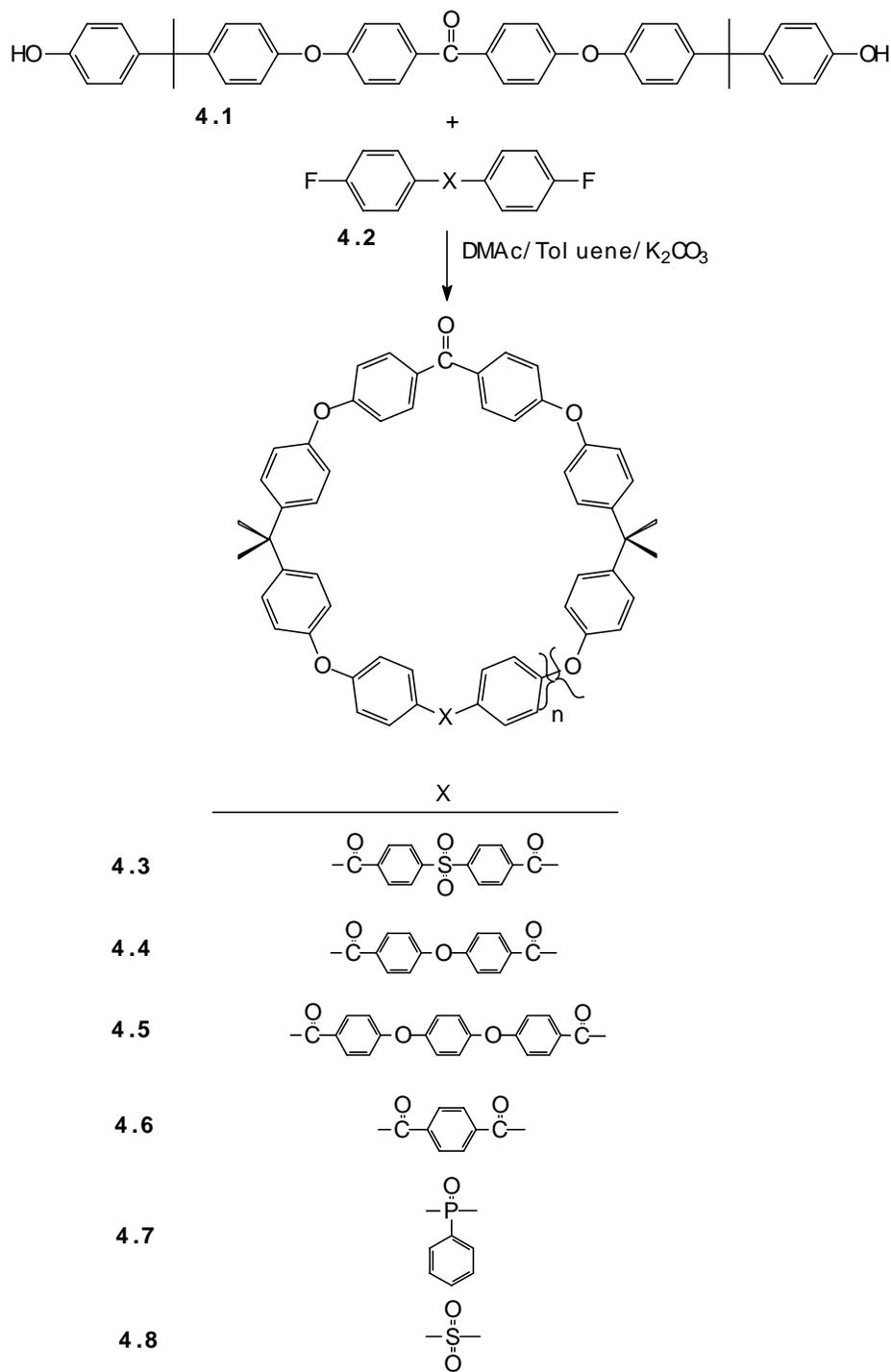
[2] Ding, Y.; Hay, A. S. *Macromolecules* **1996**, 29, 3090

[3] Cella, J. A.; Fukuyama, J.; Guggenheim, T. L. *Am. Chem. Soc. Div. Polym. Chem. Polym. Prepr.* **1989**, 30(2), 142.

Copolymerization is the most versatile technique to modify the properties of a polymer such as melting point, glass transition temperature, processibility and adhesion properties, to name a few. It was felt that analogously we can make comacrocycles, which are defined as macrocycles composed of at least two different repeating units. Comacrocyclization will result in less symmetric macrocyclic structures. In theory, this should reduce the melting points. This chapter explores the approach of comacrocyclization. The effect of the comacrocyclization on the melting point of the resulting cyclic mixtures is studied. Furthermore, the isolation of a number of pure macrocycles makes it possible to correlate the structure of a macrocycle with its melting point.

4.2 Synthesis of Comacrocycles

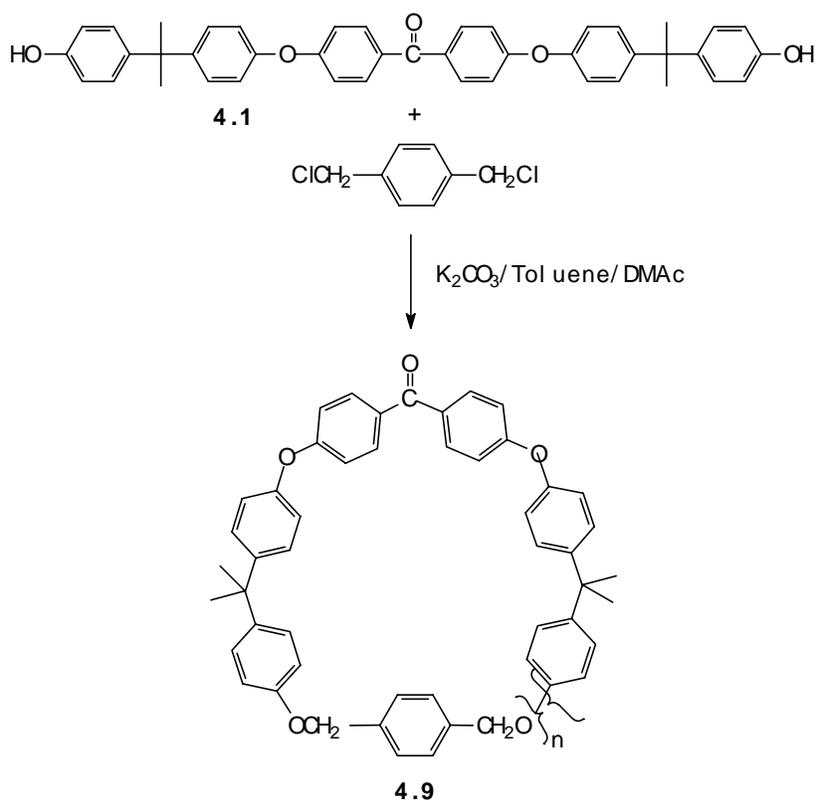
Scheme 4.1



The first series of comacrocylic mixtures were synthesized by nucleophilic aromatic substitution reactions from the extended bisphenol **4.1** reported in Chapter 2. A number of difluoro monomers were used as shown in Scheme 4.1. The difluoro monomer for cyclic mixture **4.4** was synthesized from diphenyl ether and p-fluorobenzoyl chloride. All other monomers were commercially available and used as provided. The cyclization reaction conditions were similar to those reported in previous chapters.

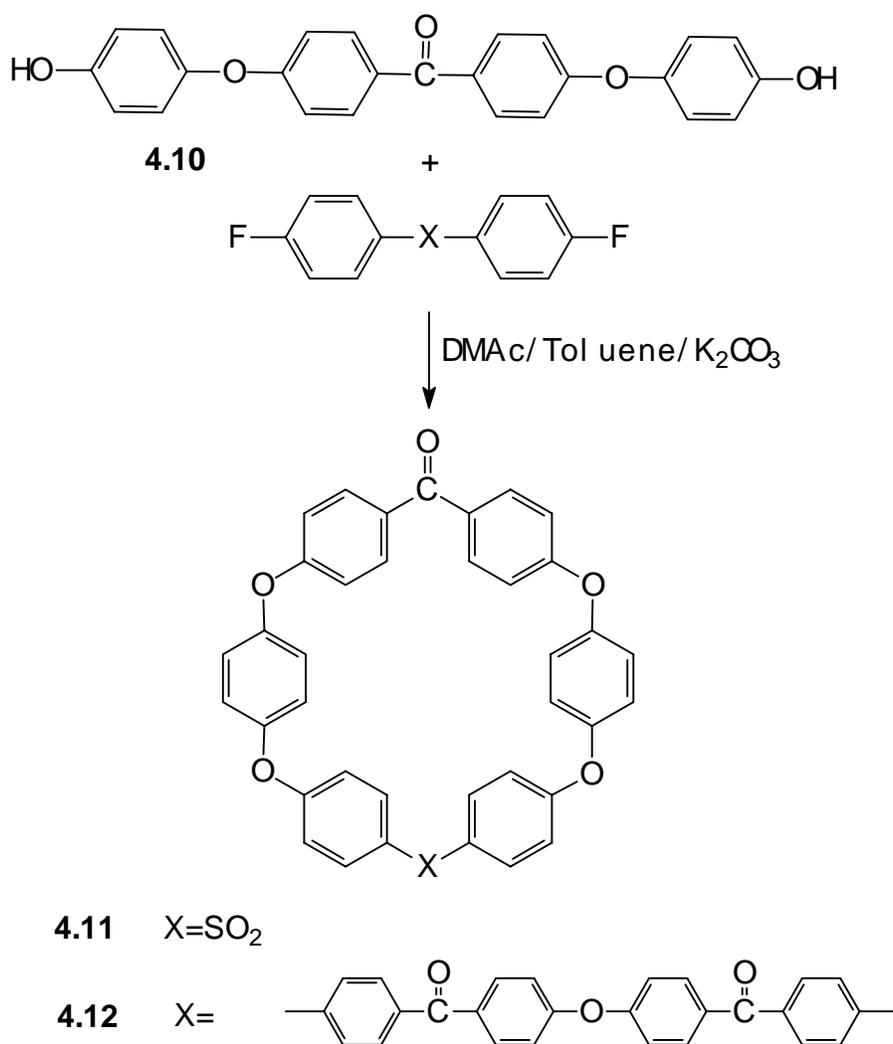
A novel macrocycle containing two benzyl groups (**4.9**) was prepared by S_N2 reaction as shown in Scheme 4.2.

Scheme 4.2



Another series of fully aromatic macrocyclic mixtures based upon the aromatic bisphenol **4.10** were synthesized according to Scheme 4.3 under similar reaction conditions. In cases in which the monomer was nearly insoluble in DMAc at room temperature, it was added in four portions over a period of 36 hours. In all other cases the reactants were added through a syringe pump to maintain the high dilution reaction conditions.

Scheme 4.3



4.3 Isolation and Characterization of Cyclic Mixtures.

Cyclic mixture **4.12** was isolated by extraction with chloroform. All other cyclic mixtures were purified by precipitating the crude products from chloroform solutions into methanol. Representative ^1H NMR spectra of these mixtures are shown in Figures 4.1-4.4. Ideally there are two types of terminal groups in linear oligomers. The phenol group signal is located around 6.77 ppm and could easily be detected in the spectra. The other is the fluoroaryl terminated group, which has a characteristic triplet at around 7.12 ppm. According to ^1H NMR spectra, there is little or undetectable amount of these groups. Therefore, all these products are close to being pure cyclics. Cyclic **4.12** is free from linear oligomers because the latter are insoluble in chloroform. All the spectra are straightforward except the cyclic mixture **4.8** containing the phosphine oxide moiety as shown in Figure 4.2. Signals beyond 7.7 ppm are due to protons ortho to the electron withdrawing carbonyl groups. Note that the sharp doublet at $\delta=7.73$ ppm is assigned to the monomeric macrocycle ($n=1$), which is approximately 26 %. Phosphine oxide is a less electron withdrawing group so protons ortho to it are located more upfield at around 7.68 ppm. The more complicated overlapped peaks are assigned to protons H_{i-h} , which are coupled with the phosphorous atom.

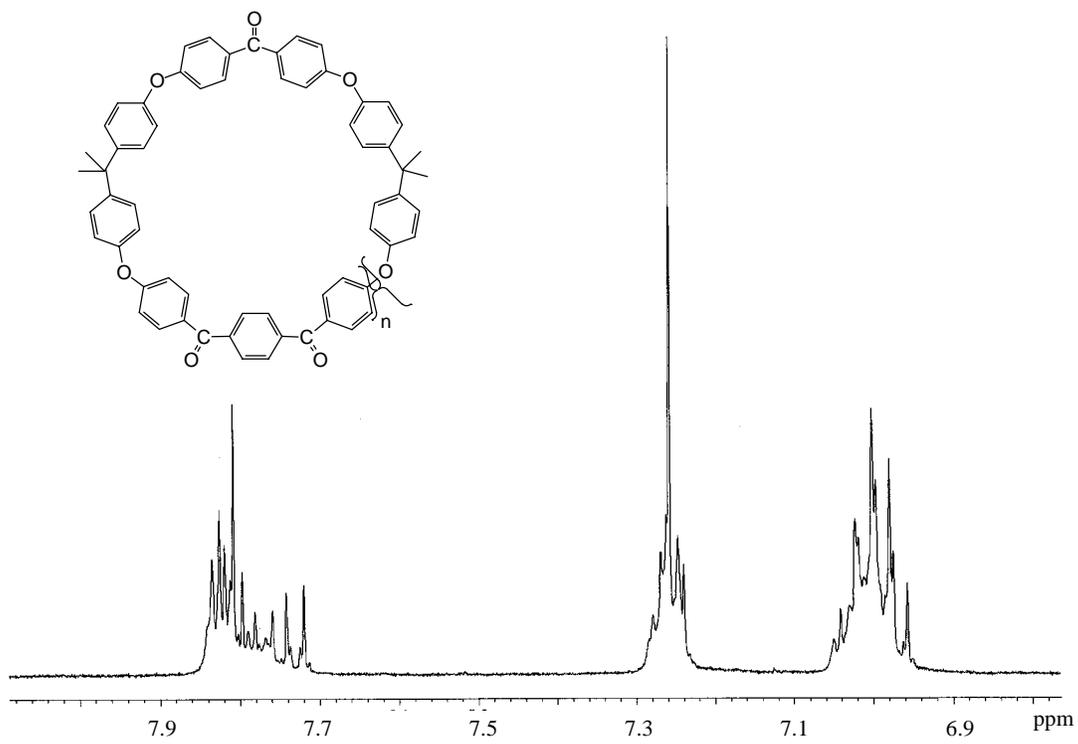


Figure 4.1. 400 MHz ¹H NMR spectrum of macrocyclic mixture **4.6** in CDCl₃,

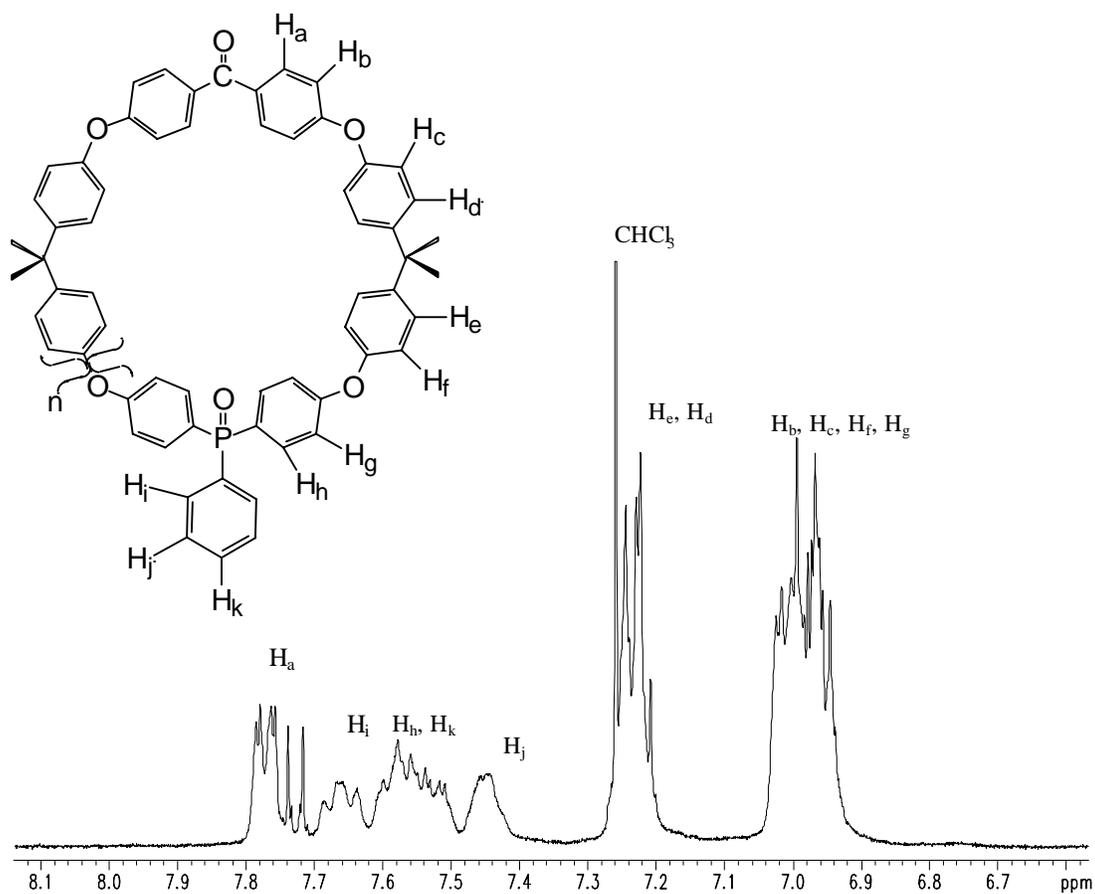


Figure 4.2. 400 MHz ^1H NMR spectrum of macrocyclic mixture **4.7** in CDCl_3 ,

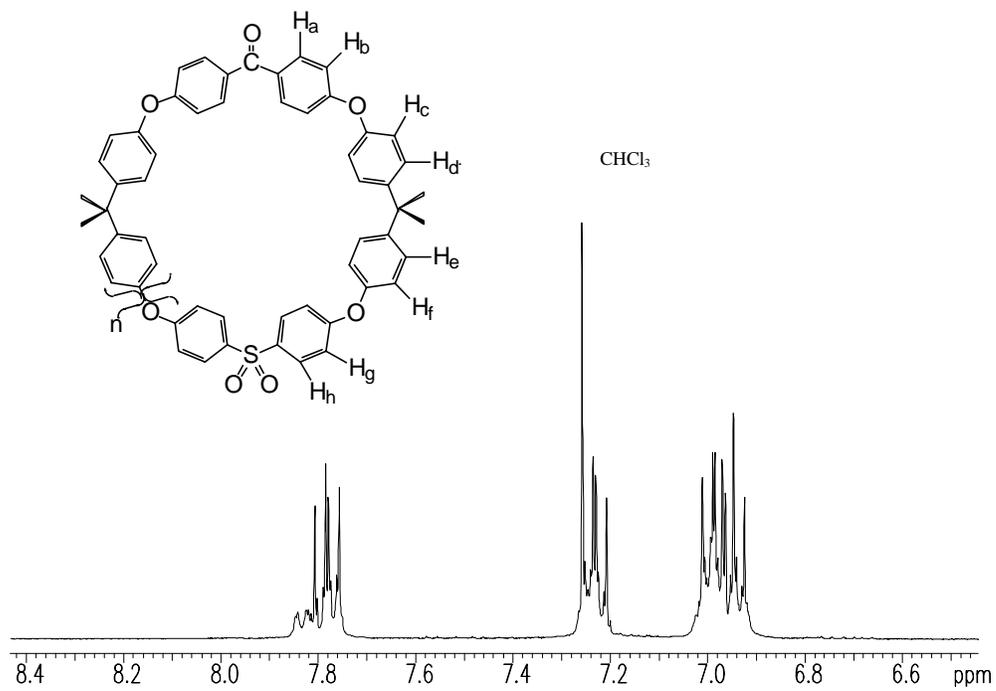


Figure 4.3. 400 MHz ^1H NMR spectrum of macrocyclic mixture **4.8** in CDCl_3 ,

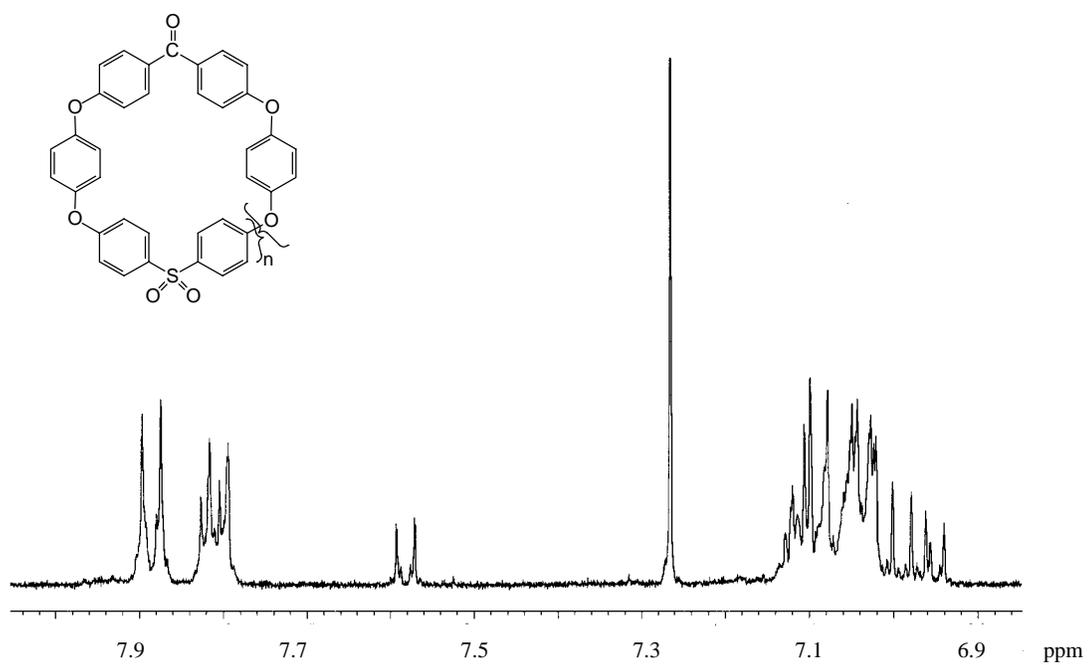


Figure 4.5. 400 MHz ^1H NMR spectrum of macrocyclic mixture **4.11** in CDCl_3 ,

The size distribution of the cyclic mixture can be seen in the GPC chromatograms, which show a number of peaks eluted towards the end (Figures 4.5-4.7). These peaks represent discrete macrocycles with different sizes, i. e., monomer, dimer, trimer etc. The size distribution strongly depends on the reactivities of the monomers. For the case of very reactive monomers such as those for cyclics **4.3** and **4.8**, the distributions are very narrow and the cyclic monomer is predominant (79 %, 68 % respectively). The 4,4'-difluorotriphenyl phosphine oxide monomer is much less reactive and the amount of cyclic monomer is quite small (26 %). For other monomers, typically the cyclics are composed of 50 % monomer, 15 % dimer and 7 % trimer with the rest being the higher oligomers. In the MALDI-TOF-MS spectrum (Figure 4.8) of cyclic mixture **4.7**, in addition to the signals for the dimer, trimer and tetramer, there are two peaks between the two consecutive cyclic oligomers. This is because the reactivity of 4,4'-difluorotriphenyl phosphine oxide monomer is quite low; the growing chain will cyclize through backbiting of the chain, thus forming macrocycles with unequal ratios of the two hetero repeating units (A and B). In the case of cyclic mixture **4.11**, according to RP-HPLC (Figure 4.9), there are a number of peaks between the dimer, trimer etc., although the ^1H NMR is very clean. This is probably due to the ring-chain equilibrium. The ether linkage is more activated by the strongly electron withdrawing sulfone group and the ether exchange process is probably relatively fast. Thus the distribution of two different hetero units is more random in the cyclic structure. Surprisingly

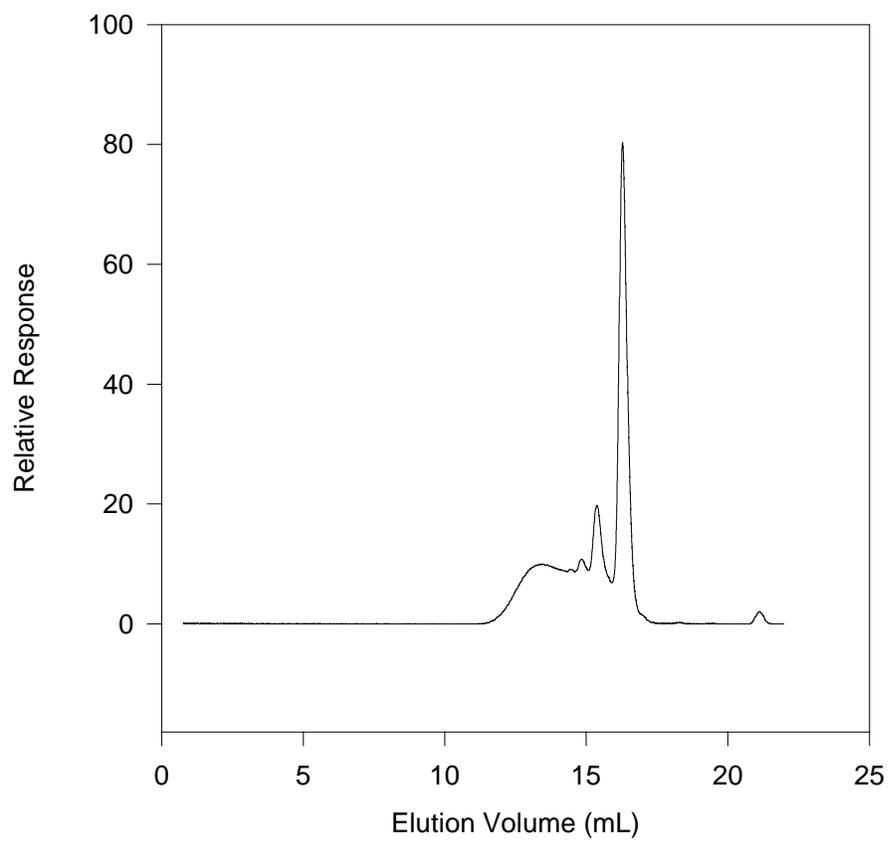


Figure 4.5. Chromatogram of cyclic mixture **4.4**.

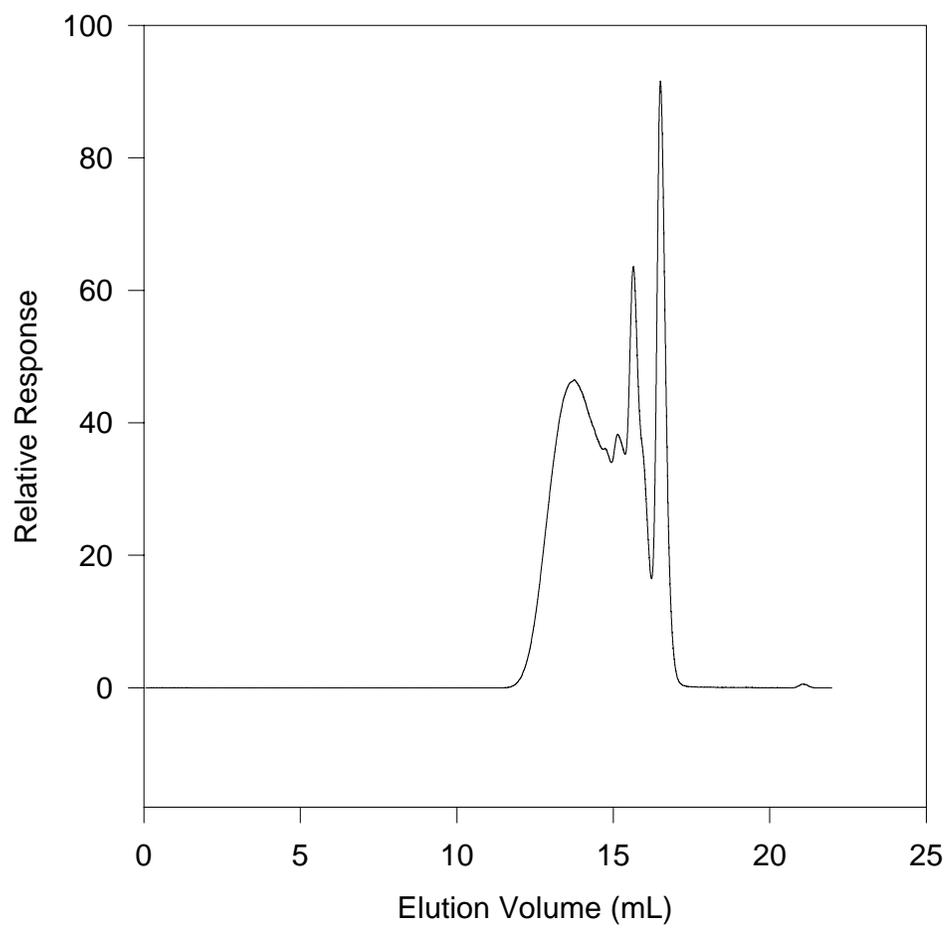


Figure 4.6. GPC chromatogram of cyclic mixture **4.7**.

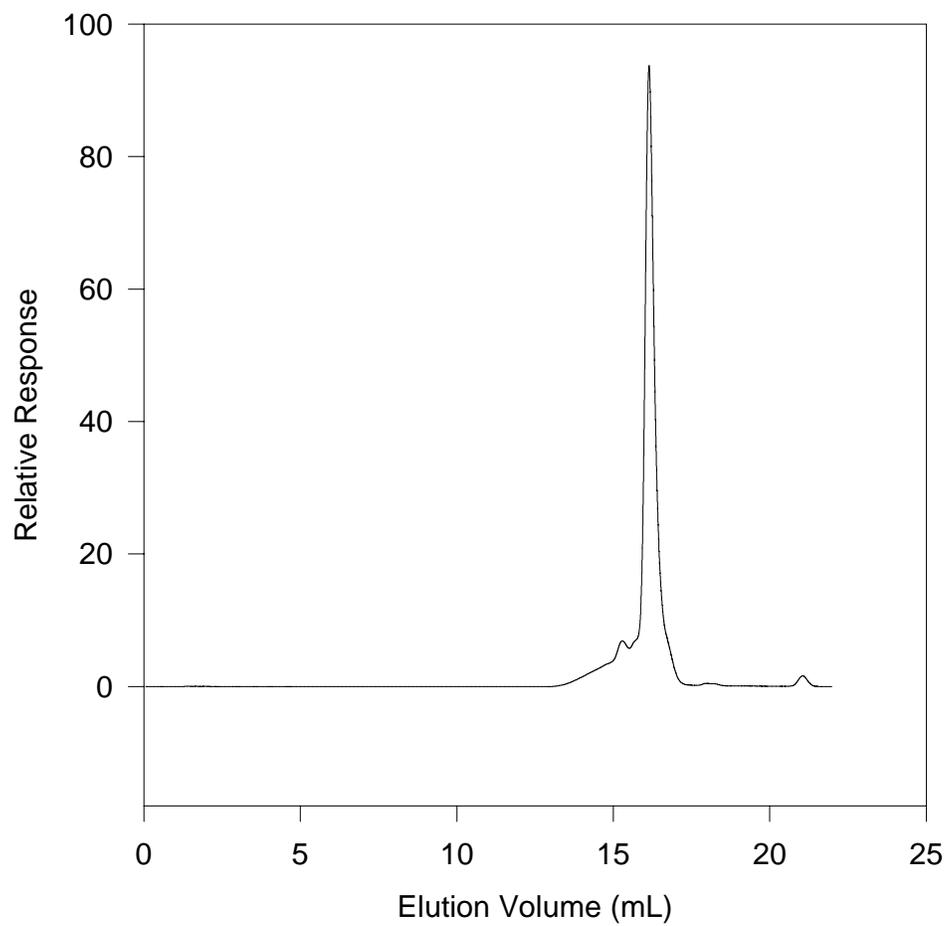


Figure 4.7. GPC chromatogram of Cyclic Mixture **4.3**.

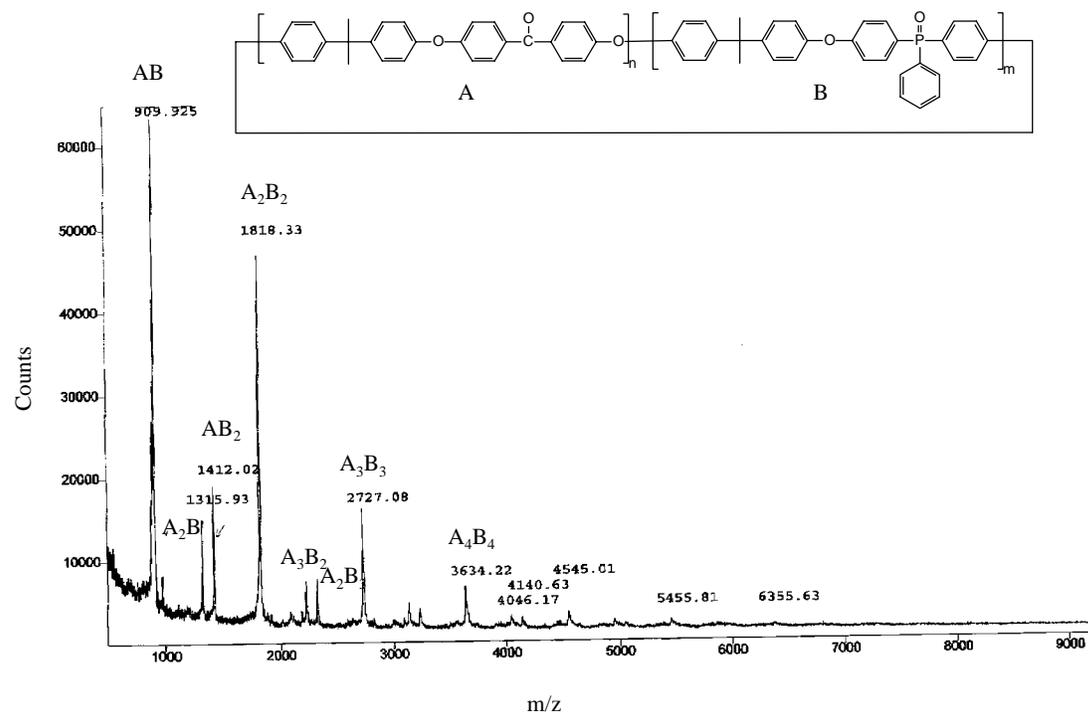


Figure 4.8. MALDI-TOF-MS spectrum of macrocyclic mixture 4.7.

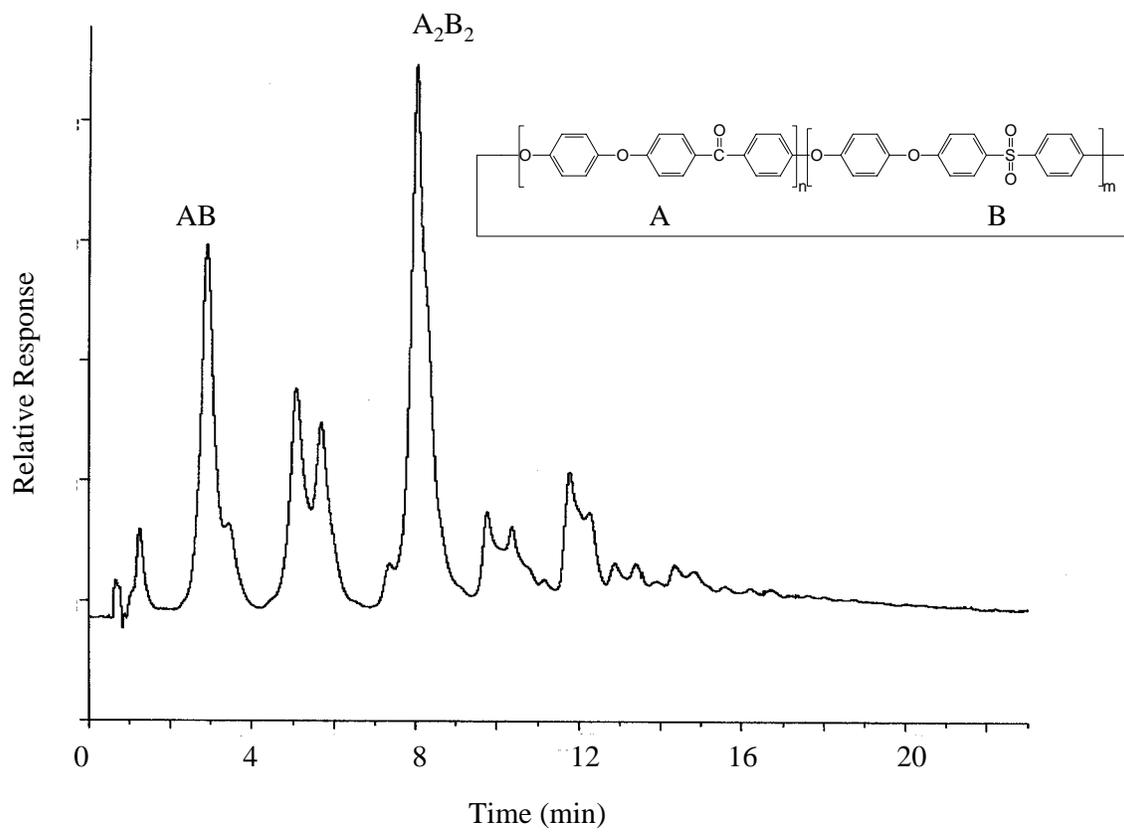


Figure 4.9. RP-HPLC chromatogram of cyclic mixture 4.11.

the cyclic monomer comprises only 21 % according to ^1H NMR, due to the ring strain of the macrocycle, which may not be formed favorably. A similar random distribution has been observed for comacrocycles¹ synthesized by reacting one activated dihalide with two different bisphenols simultaneously.

Table 4.1 Properties of Macrocylic Mixtures 4.3-4.11

Cyclic Oligomeric Mixture	Yield %	M_n^a	M_w^a	T_g^b	T_m^b
4.3	92 %	1053	2273	nd	238
4.4	89 %	1504	5654	154	320
4.5	95 %	2233	11498	154	nd
4.6	95%	1666	7596	150	nd
4.7	81 %	2028	6291	166	nd
4.8	95 %	997	2655	nd	349
4.9	75 %	930	1409	79	nd
4.11	85 %	1100	2300	nd	301
4.12	80 %	881	2433	nd	365

a. Molecular weights were measured by GPC based on polystyrene standards.

b. Thermal transition observed on the first heating of the virgin samples at 20

°C/min. nd=not detected

According to Table 4.1, the number average molecular weight corresponds to 2-3 repeating units. The average molecular weight depends on the size of the repeating units.

The DSC results for the cyclic mixtures are also listed in Table 4.1. About half of the macrocycle samples are amorphous. The others are relatively low melting point mixtures, with the cyclic mixture **4.12** having the highest melting point at 365 °C.

4.4 Isolation and Characterization of Pure Macrocycles

The isolation of the pure single sized macrocycles was done by column chromatography or by solubility differences. Representative ¹H NMR spectra of the pure single sized macrocycles are shown in Figure 4.10-11. Together with the FABMS analysis results, the structure and size of the each individual macrocycle were determined. The structures of the macrocycle along with the melting points are list in Table 4.2 (the number inside the macrocyclic structure denotes the number of ring atoms). The comparison of the structures of the macrocycles as related to the melting points illustrates the importance of the following factors. The first thing to be noticed is the effect of the symmetry. Symmetric 40-membered diketone (entry 1) has a melting point of 383 °C and the symmetric 40-membered disulfone (entry 2) has a melting point of 505 °C⁴, indicating that the sulfone group makes a macrocycle more rigid than the ketone and thus gives higher melting point. Substituting one of the ketone groups with a sulfone group, the melting point of the less symmetric macrocycle is reduced to 365 °C (entry 3), below both of the more symmetric macrocycles, even though the sulfone group tends to increase the melting point. The symmetry is reduced

[4] Colquhoun, H. M.; Williams, D. J. *Macromolecules* **1996**, 29, 3311.

more if a bulky phenyl phosphine oxide unit is introduced (entry 4). The effect is very dramatic. The melting point was reduced by 176 °C relative to entry 1. The 40-membered macrocycle in entry 5 has a melting point of 377 °C, while the more symmetric 40-membered macrocycle in entry 6 has no observable melting point because it has also one more ketone group, which contributes to the high melting point. Entries 7 and 8 represent macrocycles with small ring size (30 ring atoms), which have no observable melting points even though the symmetry of entry 8 has been reduced. The large sized 60-macrocycle (entry 9) has a melting point of 384 °C, which is still high due to the rigid sulfone groups and its symmetry. The 37-membered macrocycle (**4.9**, **n=1**) (entry 11) has a very low melting point, thanks to the flexible benzyl ether units. Interestingly, according to its single crystal X-ray structure (Figure 4.12), one CH₂ group is pointing inside of the macrocycle and the other is pointing towards the outside of the macrocycle; thus the conformation in the crystal structure is unsymmetric. The macrocycle in entry 10 has a relative large ring size and less symmetric structure; thus its melting point is relatively low (310 °C).

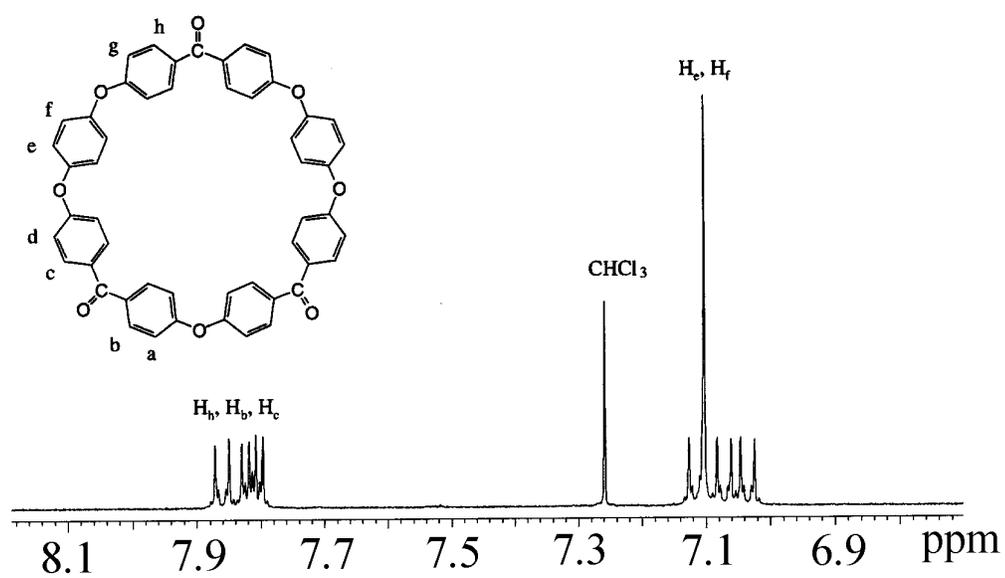


Figure 4.10. 400 MHz ¹H NMR spectrum of macrocyclic monomer **4.12** (n=1) in CDCl₃.

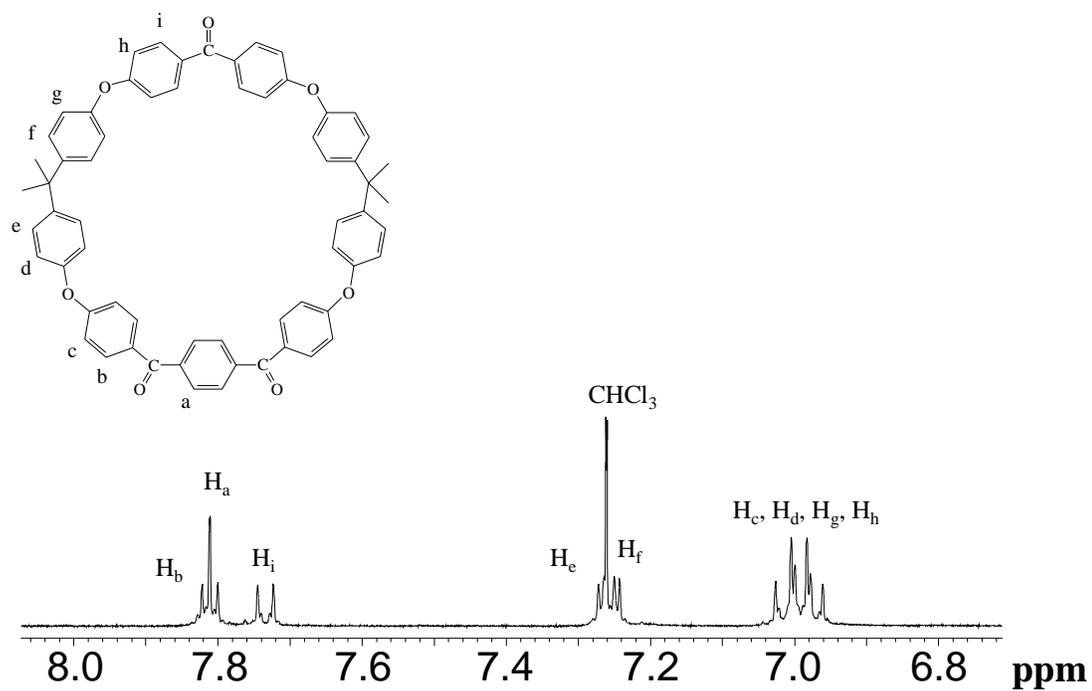
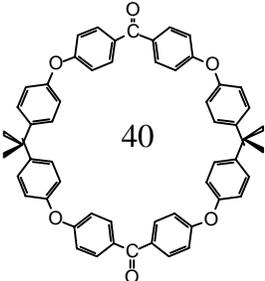
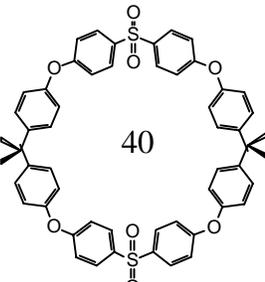
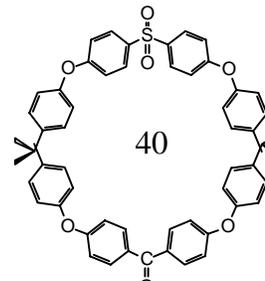
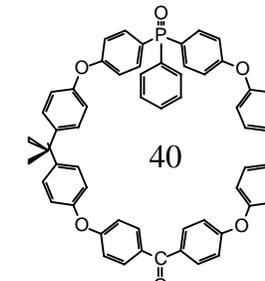
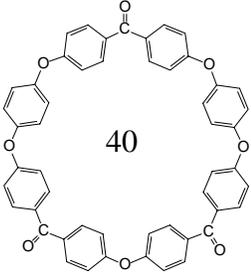
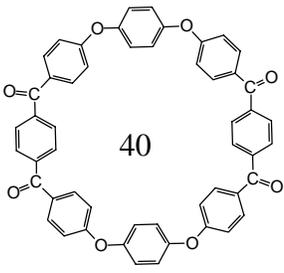
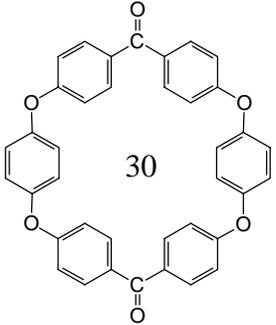
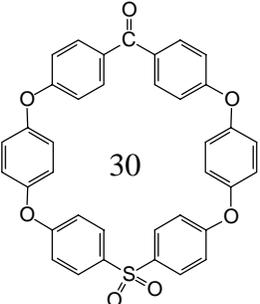


Figure 4.11. 400 MHz ^1H NMR spectrum of macrocyclic monomer **4.6** (n=1) in CDCl_3 .

Table 4.2. Melting points of pure single sized macrocycles.

Entry	Structure	T_m (°C)
1		386
2		505
3		365
4		210

continued

Entry	Structure	T _m (°C)
5		377
6		>440
7		>440
8		>440

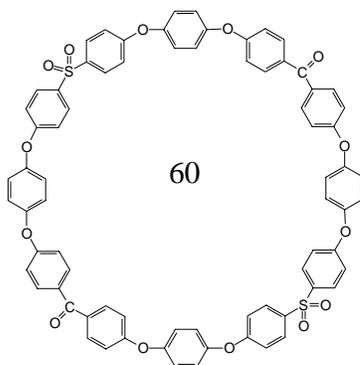
Continued

Entry

Structure

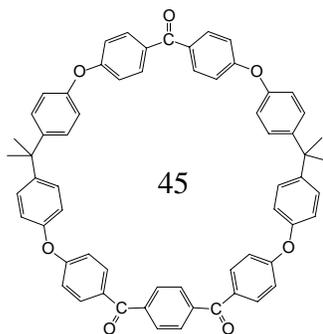
T_m (°C)

9



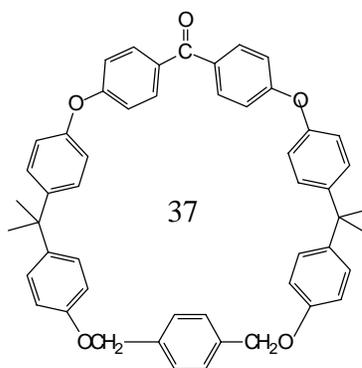
384

10



310

11



241

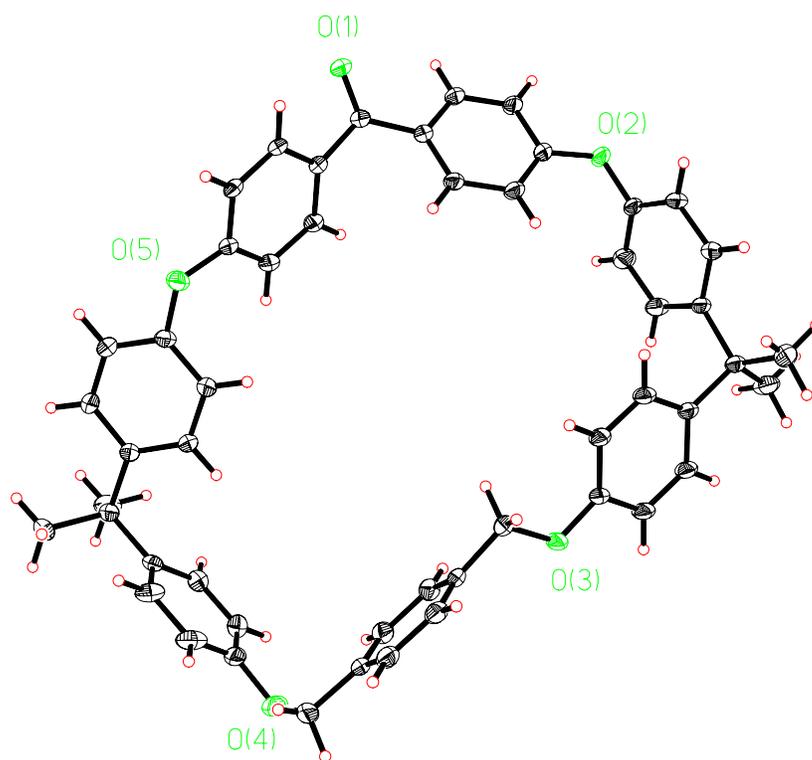


Figure 4.12. Single crystal X-ray structure of macrocyclic monomer **4.9** (n=1).

4.4 Conclusions

1. A number of comacrocylic mixtures were synthesized and some of the pure small sized macrocycles were isolated and characterized by various techniques.
2. The monomer repeating units in the macrocycles are not strictly one to one due to the backbiting competition reaction in the case of low reactivity monomers and ring-chain equilibria.
3. Comacrocyclization reduces the melting points significantly compared with homomacrocyces.
4. Breaking the symmetry of the macrocycle effectively reduced the melting points of the smallest macrocycle, and thus the cyclic mixtures as a whole. The melting points of single sized macrocycles are controlled by a number of factors, i. e., ring size, number and nature of functional groups and the symmetry. These three factors are of equal importance. The effect of functional groups on the melting point is in the order of $\text{SO}_2 > \text{CO} > \text{ether}$.

4.5 Experimental

Materials

All the materials were used as received. 4,4'-Difluorodiphenyl sulfone and α, α' -Dichloro-p-xylene were provided by Aldrich. DMAc and toluene were supplied by Fisher. 4, 4'-Bis(p-fluorobenzoyl)phenyl sulfone was provided by Jim Yang. 4, 4'- Bis(4-fluorobenyoyl)benzene and 4, 4'-difluorophenyl phosphine oxide were kindly provided by Dr. McGrath's group at Virginia Tech.

Measurements

Melting points were determined on a Haake-Buchler capillary melting point apparatus and were corrected. NMR experiments were performed at room temperature on a Varian Unity 400 MHz NMR Spectrometer using tetramethylsilane as the internal standard. The X-ray structure was provided by Dr. Guzei of Prof. Rheingold's group at the University of Delaware. HPLC and GPC conditions were reported in the experimental part of Chapter 3. MALDI-TOF-MS spectra were provided by Mass Spectroscopic Center at Washington University at Saint Louis.

Synthesis of 4-fluorobenzoylphenyl ether.

p-Fluorobenzoyl chloride (5.00 g, 31.5 mmol) and anhydrous AlCl_3 (5.04 g, 37.8 mmol) were added to 20 mL methylene chloride (dried over P_2O_5) in a 250 mL round flask with a magnetic stirrer, a condenser and N_2 inlet-outlet. Diphenyl ether (2.28 g, 13.4 mmol) dissolved in 20 mL methylene chloride was added from

a dropping funnel. The mixture was refluxed for an hour and kept overnight at room temperature. The product precipitated out. The mixture was quenched in ice-water and concentrated HCl, which was washed with water and the solvent was removed under vacuum to get a solid. The solid was washed with acetone. Yield 5.0 g (91 %); mp 221.8-224.5 °C (lit.²⁷ mp 223-225 °C); IR: 1643, 1596, 1503, 1310, 1238, 766; ¹H NMR (400 MHz, CDCl₃): δ=7.86 (d, 4H, J=8.8 Hz), 7.84 (dd, J=8.8 Hz, J=8.8 Hz, 4H), 7.18 (t, J=8.8 Hz, 4H), 7.15 (4H, J=8.8 Hz).

General Procedures for the synthesis of comacrocycles

To a 500 mL round bottom flask equipped with a magnetic stirrer, a Dean-Stark trap, N₂ inlet and outlet were added 250 mL DMAc and 100 mL toluene. The system was azeotropically refluxed for 3 hours and the temperature was adjusted to 155 °C by removing about 70 mL toluene. Then 30 mL solvent was taken from the flask to dissolve 5 mmol each monomer and the solution was injected at a rate of 1 mL/h into the flask suspended with K₂CO₃ (0.828 g, 6 mmol). The total reaction time was about 60 hours. Solvent was removed under vacuum and the solid was washed with water to remove the salts. The product was dissolved in about 15 mL chloroform and precipitated into 30 mL methanol. The solid product was filtered and dried in a vacuum oven overnight at 100 °C. Pure single sized macrocycles were isolated by column chromatography on silica gel with methylene chloride.

[27] Kricheldorf H. R.; Delius, U. *Macromolecules* **1989**, 22, 517.

Chapter 5

Synthesis of Macrocyclic Monomers by Friedel-Crafts Acylation Cyclization

5.1 Introduction

The recent discovery by Brunelle and coworkers 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 aspects, 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, amides, ether imides, ether ketones, and ether sulfones.

Although the Friedel-Crafts acylation polycondensation reaction has been used to make poly(ether ketone)s,¹⁻³ there has been no report of the synthesis of cyclic oligo(ether ketone)s using the same reaction. We were interested in

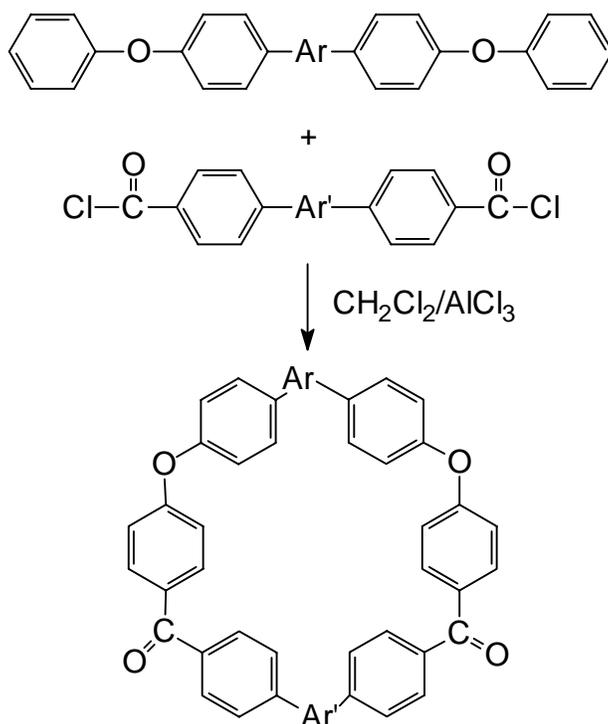
[1] Staniland, P. A. "Comprehensive Polymer Science", Pergamon press, New York, **1989**, Vol. 5, pp. 443-497.

[2] Mullins, M. J.; Woo, E. P. J. *Macromol. Chem. Phys.* **1987**, C27(2), 313.

[3] Jansons, V.; Dahl, K. *Makromol. Chem., Macromol. Symp.* **1991**, 51, 87.

exploring the feasibility of generating macrocycles by the Friedel-Crafts acylation reaction. There are several potential advantages of using this reaction for the synthesis of macrocycles. First, the reaction is generally very fast, which is favorable for maintaining the pseudo-high dilution condition, and thus producing high yields. Secondly, the reaction temperature is relatively low, e. g., room temperature. In addition, the typical acylation solvents, such as methylene chloride, are inexpensive. This chapter deals with the possibility of making macrocycles by Friedel-Crafts acylation. The synthesis can be generalized in Scheme 5.1, which involves a diphenoxy terminated precursor and a diacid chloride.

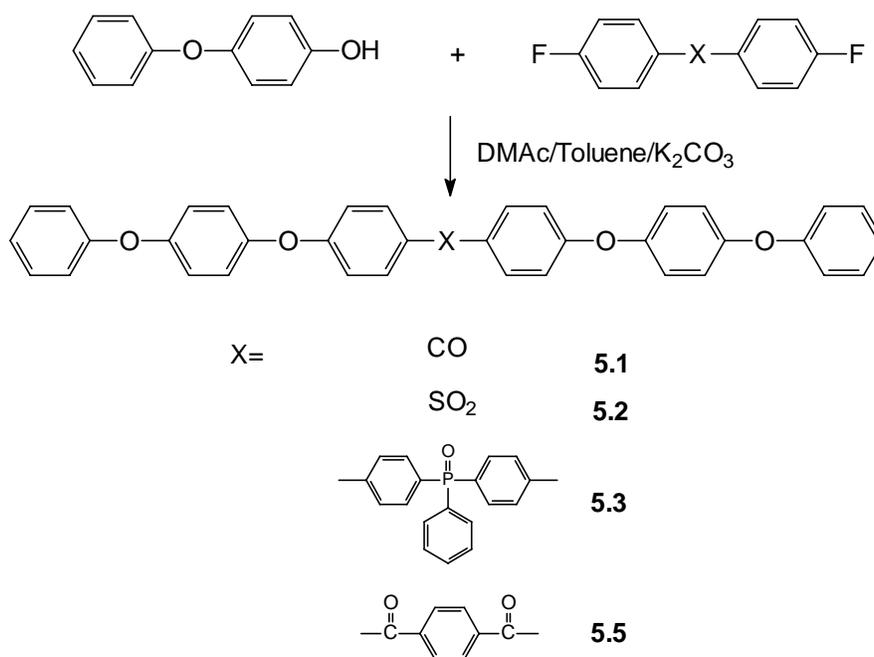
Scheme 5.1



5.1 Synthesis of Precursors

As with our previous approach, long precursors were synthesized first. The syntheses of diphenoxy terminated precursors were straightforward. A number of these precursor were synthesized in almost quantitative yield by nucleophilic aromatic substitution reactions from 4-phenoxyphenol or phenol and activated dihalides as outlined in Scheme 5.2. The ^1H NMR proved formation of these compounds (Figure 5.1).

Scheme 5.2



Diacid chloride precursor **5.8** was reported by Idage and coworkers⁴. We found that it can be more conveniently synthesized using the more

[4] Idage, S. B.; Idage, B. B.; Shinde, B. M. *J. Polym. Sci., Polym. Chem. Ed.*

1989, 27, 583.

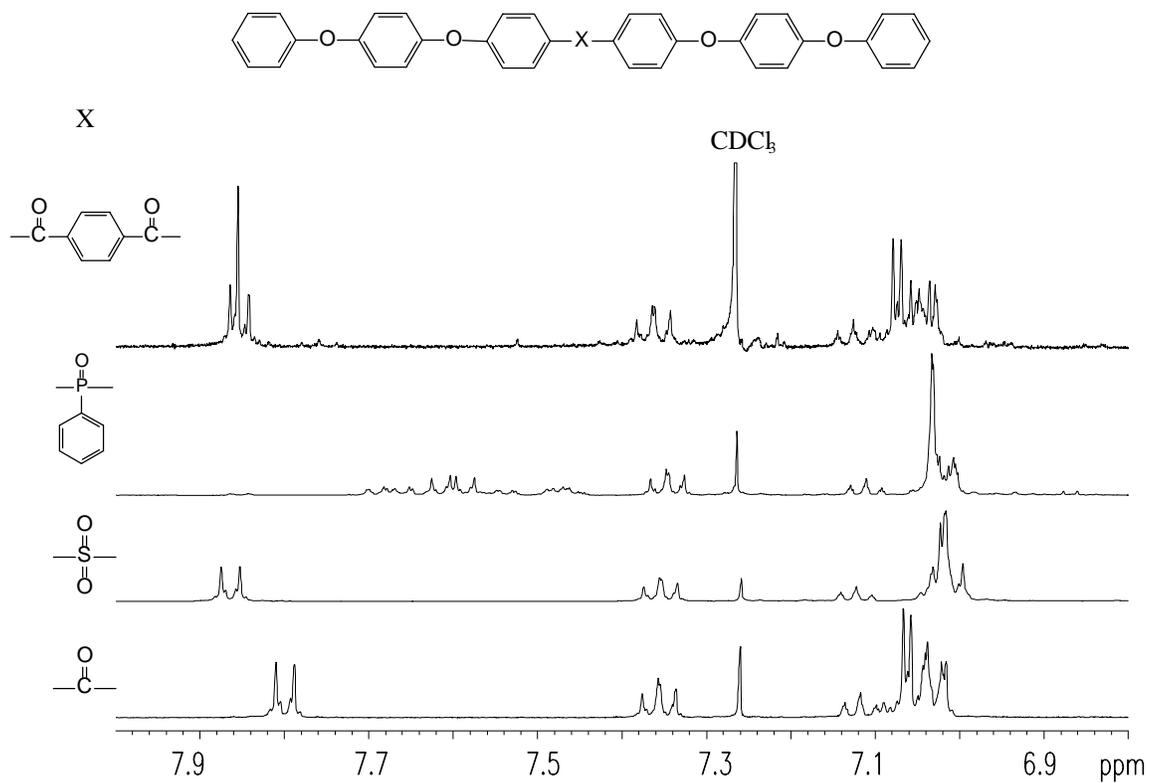
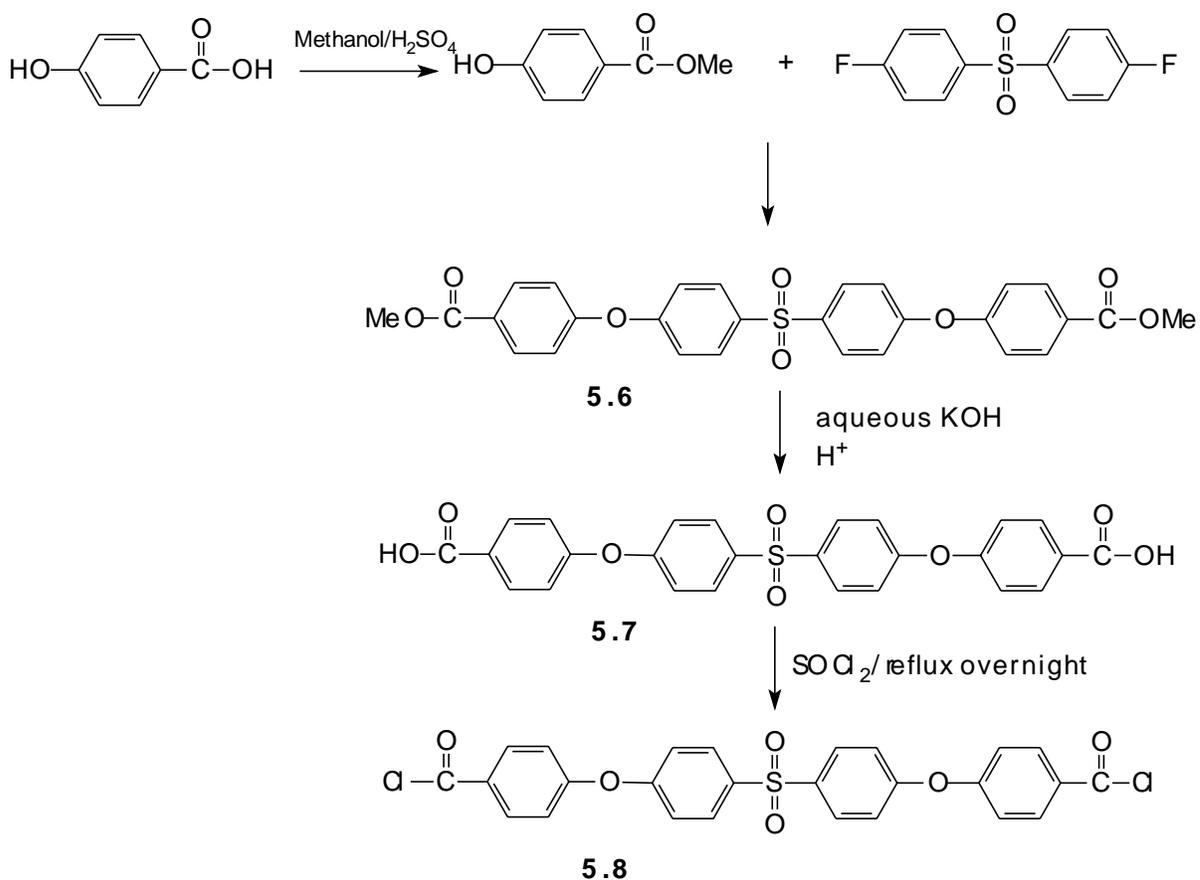


Figure 5.1. 400 MHz NMR ¹H NMR spectra of phenoxyphenoxy terminated precursors in CDCl₃.

reactive 4, 4'-difluorodiphenyl sulfone (Scheme 5.3). Direct synthesis of **5.7** using 4-hydroxybenzoic acid did not give a clean product. Instead, methyl 4-hydroxybenzoate was used. Compound **5.6** was obtained in almost quantitative yield. Clean product was not obtained if less expensive 4,4-dichlorodiphenyl sulfone was used because of the low reactivity. Hydrolysis of **5.6** in aqueous KOH afforded the diacid **5.7**, which was easily transformed into the diacid chloride **5.8** with thionyl chloride. The ^1H NMR spectrum showed the correct structure (Figure 5.2)

Scheme 5.3



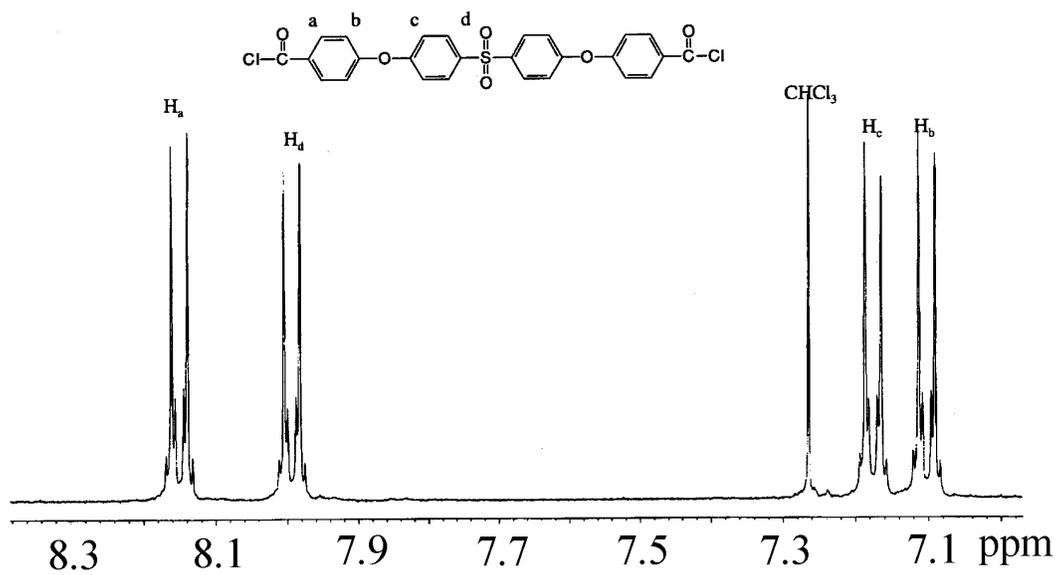
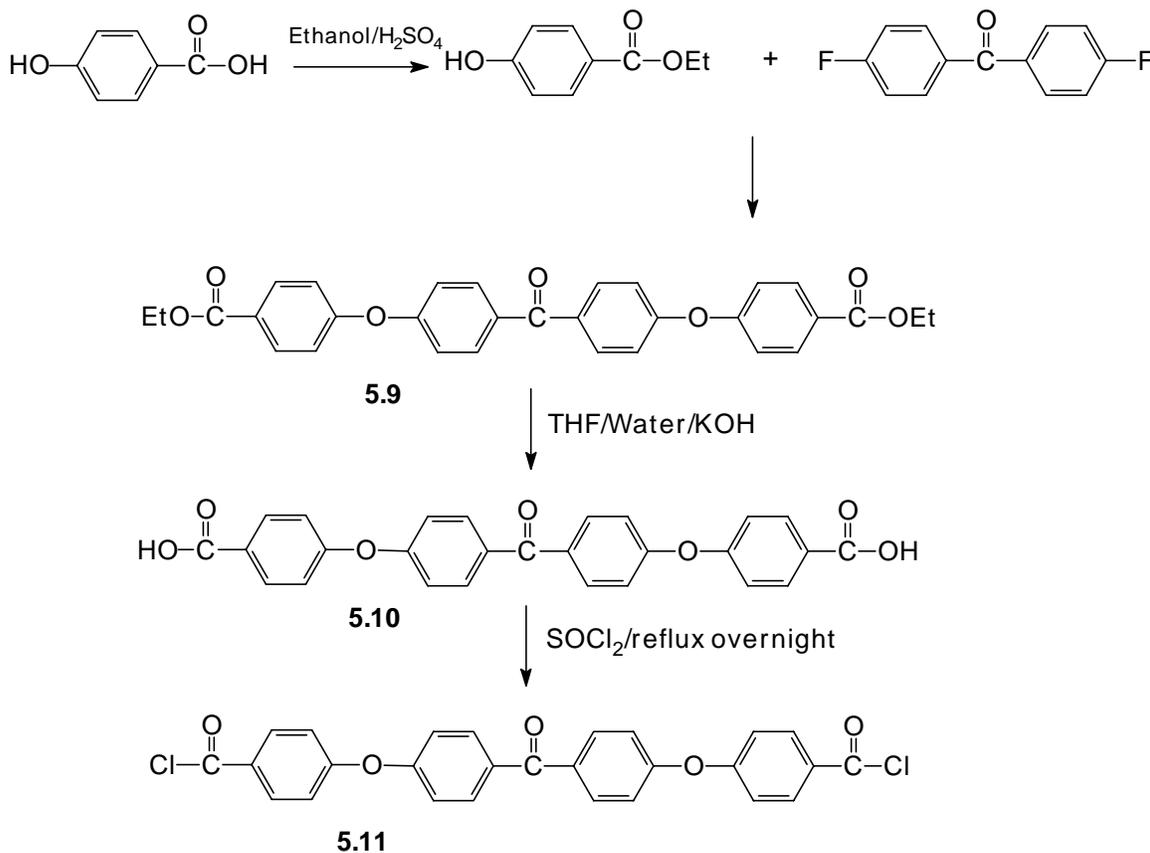


Figure 5.2. 400 MHz ¹H NMR spectrum of diacid chloride **5.8** in CDCl₃.

Scheme 5.4



The synthesis of similar compound **5.11** was more difficult. 4-Hydroxybenzoic acid was reacted with 4,4'-difluorobenzophenone directly in an attempt to make **5.10**. Instead of getting the desired product, 4,4'-diphenoxybenzophenone was isolated by extraction with acetone as indicated by TLC and its NMR spectrum. This was probably due to the decarboxylation of the 4-hydroxybenzoic acid to phenol, which then reacted with 4,4'-difluorobenzophenone to form the product. An attempt to minimize the side reaction at low reaction temperature (127 °C) was not successful. Therefore, 4-hydroxybenzoic acid was protected as a methyl ester. During the reaction with 4,4'-difluorobenzophenone, precipitation of the product was noticed. After 45

hours of reaction, the isolated product was not the desired one. ^1H NMR of the soluble part of the product suggested the reaction was incomplete. The other insoluble part was probably the desired product. However, it is insoluble in common organic solvents such as acetone, chloroform, DMSO and DMAc and can not be characterized. It was felt that increasing the length of the aliphatic group probably would increase the flexibility and the solubility problem could be avoided. Thus ethyl benzoate was used in 10 % excess to balance the stoichiometry because it can be self condensed to form polybenzoate. Insoluble polybenzoate was filtered from the chloroform solution. After recrystallization in DMAc, pure product **5.9** was obtained in 58 % yield. Hydrolysis of **5.9** in aqueous KOH was attempted first. After several days, there was not any sign of hydrolysis. This is because there is little solubility of the compound in water and diacid **5.10** is also insoluble. It was found that hydrolysis occurred in aqueous THF, however very slowly. After several days, the product was isolated as an insoluble salt. It was acidified with aqueous HCl, despite the fact that it is insoluble in water. Then it was reacted with thionyl chloride to form **5.11**, which was purified by recrystallization in toluene to give the final product in 72% yield. The NMR spectrum of **5.11** has the characteristic four doublets, which are consistent with its structure (Figure 5.3).

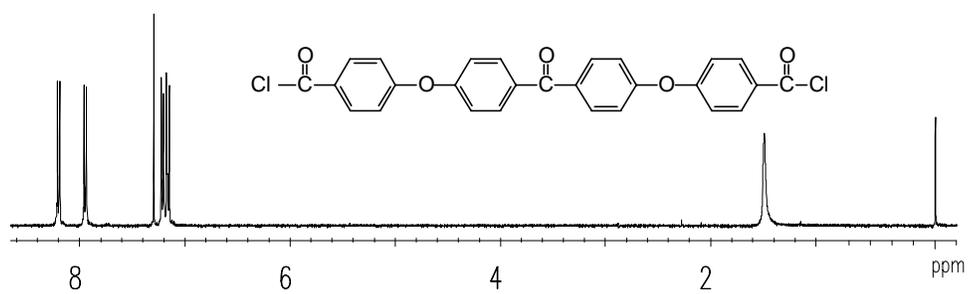
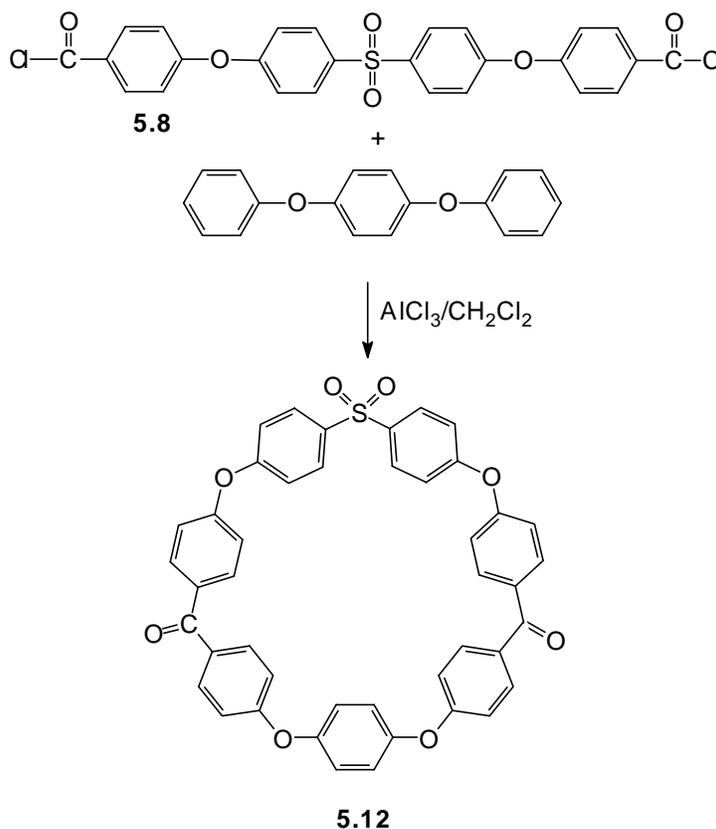


Figure 5.3. 400 MHz ^1H NMR spectrum of diacid chloride **5.11** in CDCl_3 .

Another diacid chloride, i. e. 4,4'-oxybenzoyl chloride, was synthesized from the corresponding 4,4'-oxybenzoic acid with thionyl chloride and purified by recrystallization in toluene.

5.3 Cyclization Reaction

Scheme 5.5



The Friedel-Crafts acylation cyclization was carried out in methylene chloride. Because of the large amount of solvent used, hydrolysis of the acid chloride was a concern. Methylene chloride was distilled over P_2O_5 prior to use. In the typical procedures, 3.5 Equivalents of AlCl_3 were suspended in methylene chloride. The large excess of AlCl_3 was intended to increase the solubility of the growing chain. Reactants dissolved in methylene chloride were

added dropwise into the flask within about 3 hours to maintain the pseudo-high dilution conditions. A syringe pump was not used because of easy evaporation of the solvent and the piston got stuck. The reaction continued for about 12 hours. During the reaction, a red brown precipitate was noticed. The crude product was isolated by extraction with an appropriate solvent, typically chloroform. In some cases, hydrolysis of the acid chloride was noticed as the NMR signal of the diacid was seen in the crude product. This impurity was easily removed by treating the crude product with potassium hydroxide.

The first macrocycle attempted was 35-membered macrocycle **5.12** containing ether ketone and ether sulfone linkages (Scheme 5.5). After the reaction, the crude product was isolated by exhaustive extraction with hot acetone. Pure **5.12** was obtained using a silica gel column eluted with methylene chloride.

Figure 5.4 gives the ^1H NMR spectrum of macrocycle **5.12**. 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. In the ^{13}C NMR spectrum, the carbonyl carbon is located at $\delta=193.3$ ppm and the total number of peaks is 15, which is consistent with the structure of the macrocycle. The EI

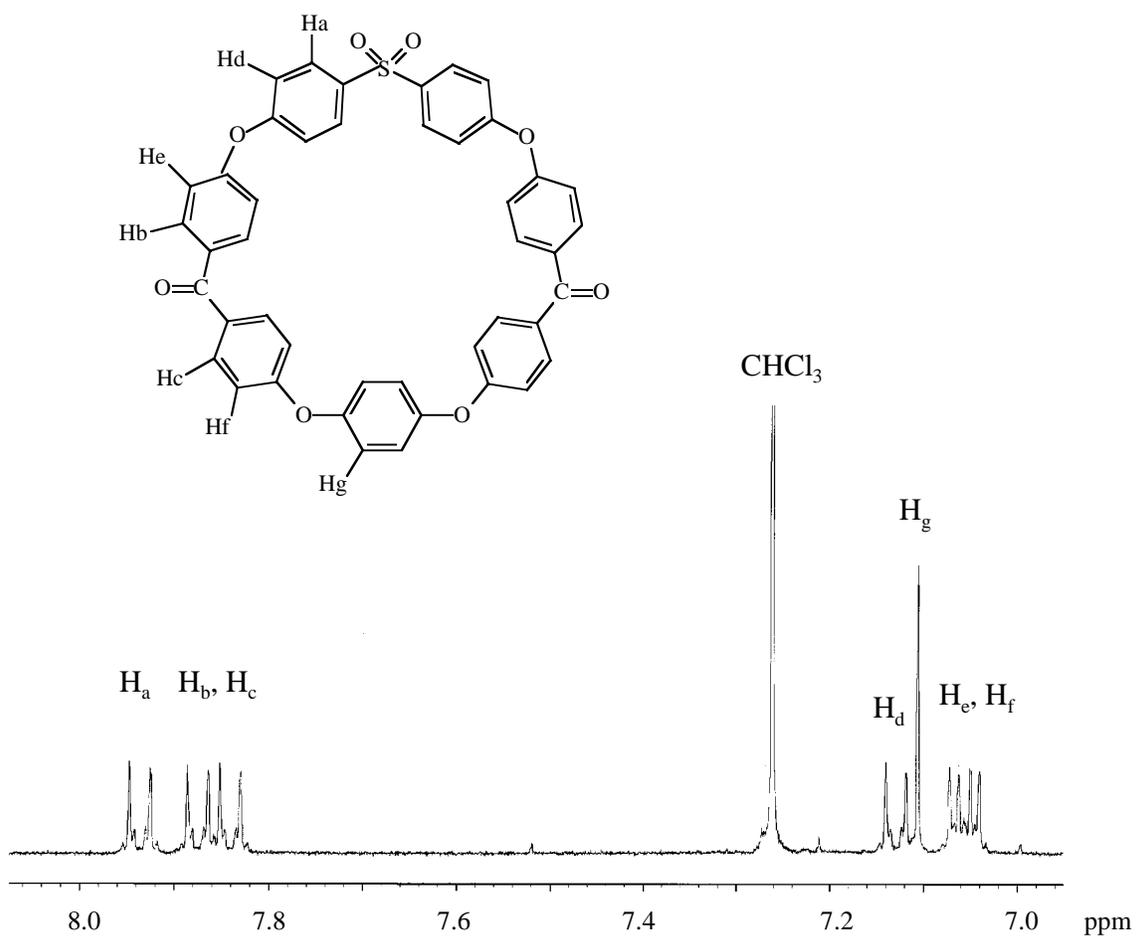


Figure 5.4. 400 MHz ^1H NMR spectrum of 35-membered macrocycle **5.12** in CDCl_3 .

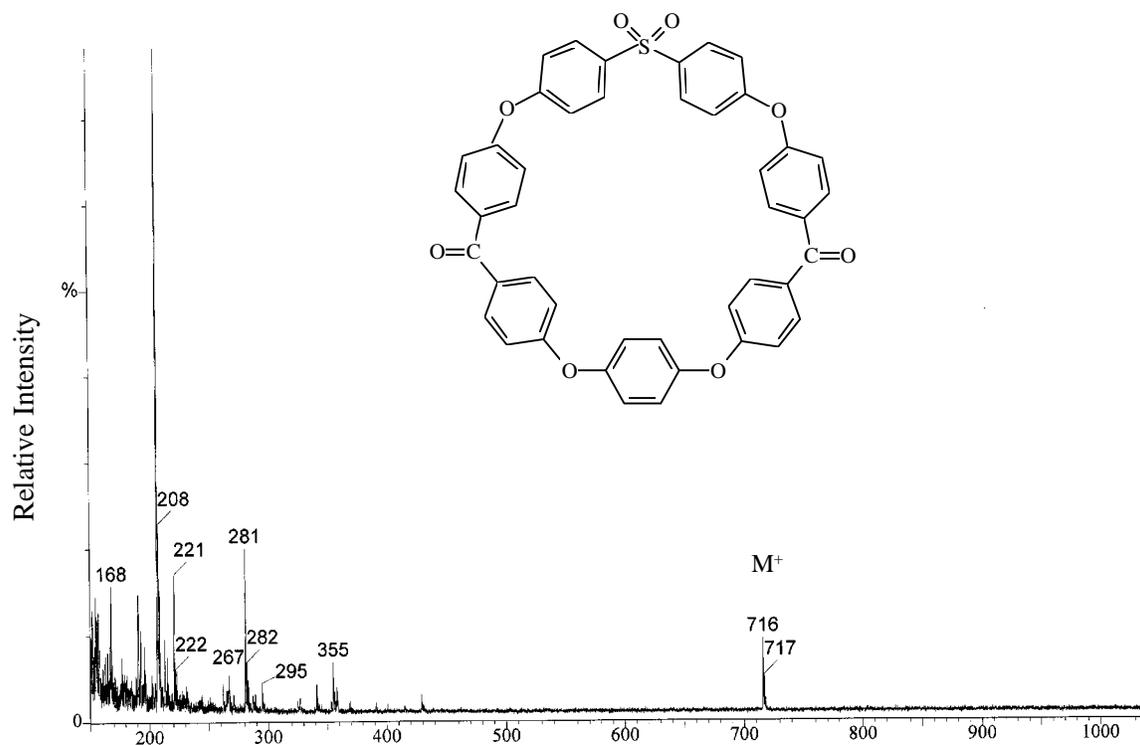


Figure 5.5. Electron impact mass spectrum of 35-membered macrocycle **5.12**.

mass spectrum (Figure 5.5) of the macrocycle shows the correct molecular ion peak at $M^+=716$ (calculated 716.15). The X-ray structure⁵ conclusively confirmed its cyclic structure (Figure 5.6). This macrocycle adopts a rigid and open conformation.

The yield (21 %) was quite low compared with similar macrocycles from nucleophilic aromatic substitution reactions. There are several reasons accounting for this. First, the high dilution condition was not well maintained. The reactants were added in a period of about 3 hours instead of well controlled addition rate over a period of 36 hours. The second reason is the poor solubility of the growing chain. Presumably the linear oligomers precipitated during the reaction, preventing further cyclization to form large sized macrocycles. In the acetone extract, there was no evidence of the double sized macrocycle formed in the FABMS experiment. In the MALDI-TOF-MS, there was a very weak signal for the double sized macrocycle. It is an indication that linear oligomers with more than one repeating unit will probably precipitate out from the solution.

[5] The single crystal was grown from THF solution by vapor diffusion method. Due to the 6 disordered THF molecules in the crystal lattice, the R value is high. But correct connection was confirmed from the X-ray analysis.

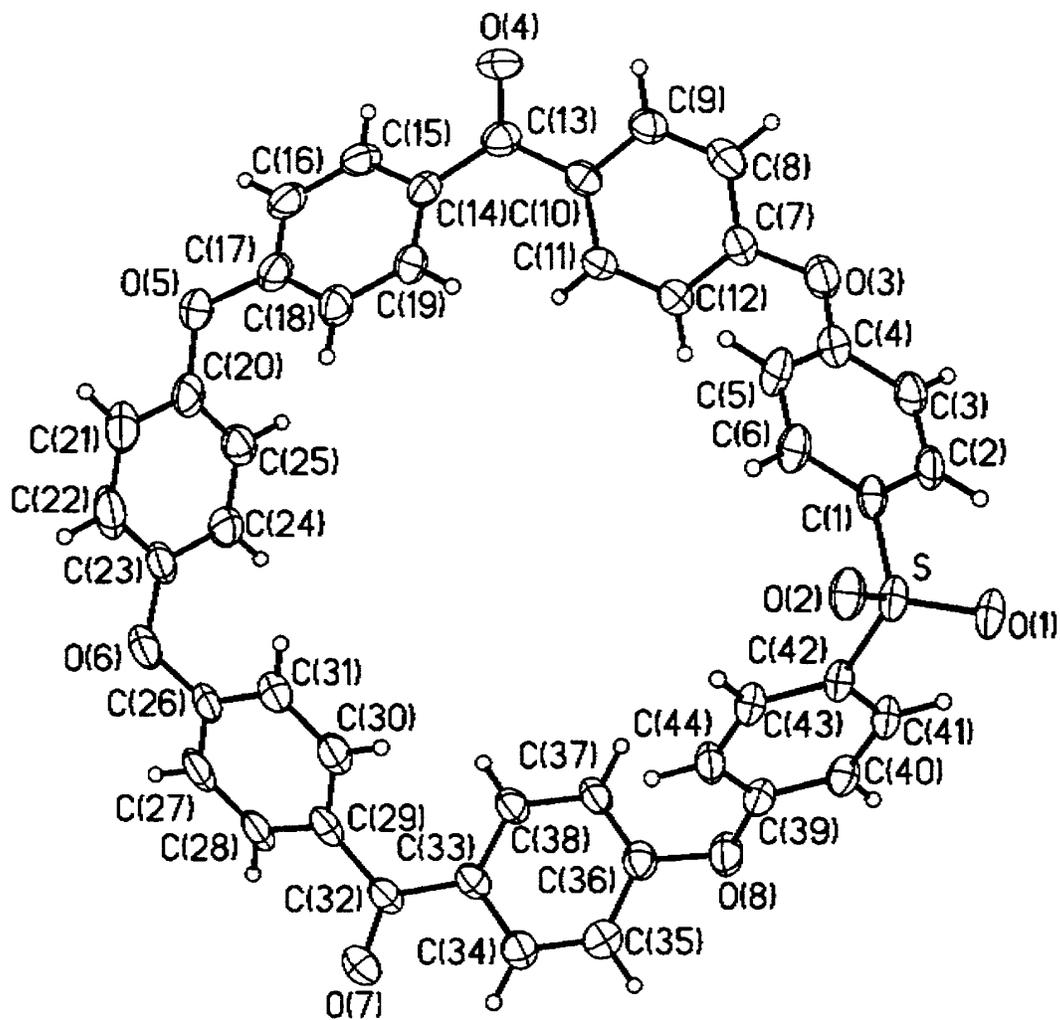


Figure 5.6. Single crystal X-ray structure of 35-membered macrocycle **5.12**.

The next attempted Friedel-Crafts acylation cyclization is shown in Scheme 5.6. The cyclization conditions were similar. Again, the product precipitated out during the reactions. This time the cyclic mixture was isolated by extraction with chloroform to get a yield of 9%. This is an even lower yield. Interestingly, the same cyclic mixture can be obtained by nucleophilic aromatic substitution reaction from hydroquinone and a difluoroketone compound 5.15. The yield from nucleophilic aromatic cyclization reaction was 32%, which is not very high, but much higher than the yield from the Friedel-Crafts acylation reaction.

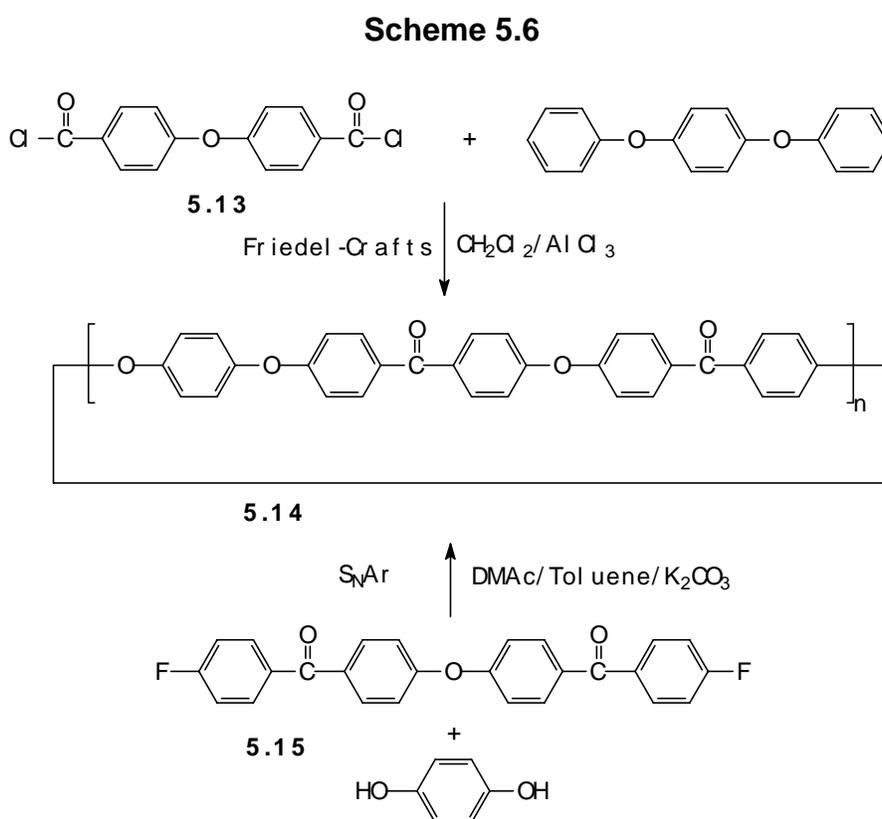
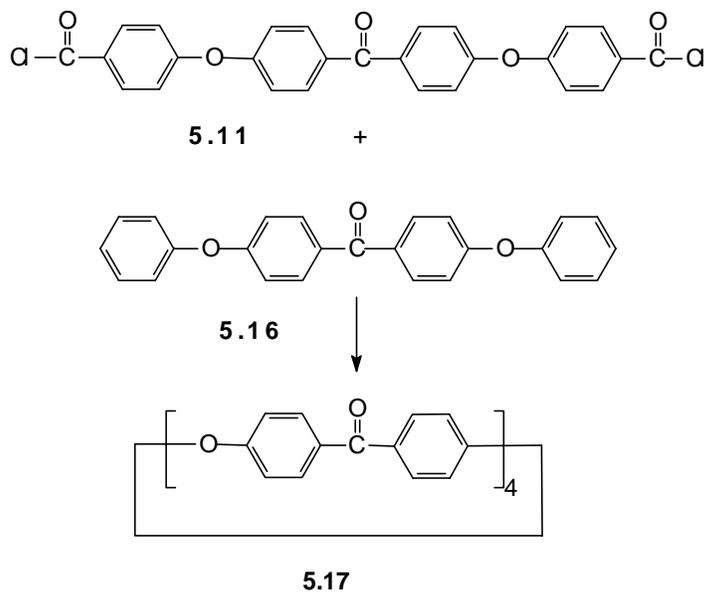


Figure 5.7 compares the ^1H NMR spectra of macrocyclic mixtures synthesized by the two different methods. It appears that there is not much

difference between the two. The mixture obtained from S_NAr reaction appears to be purer.

A cyclic monomer for poly(ether ketone) was synthesized according to Scheme 5.7.

Scheme 5.7



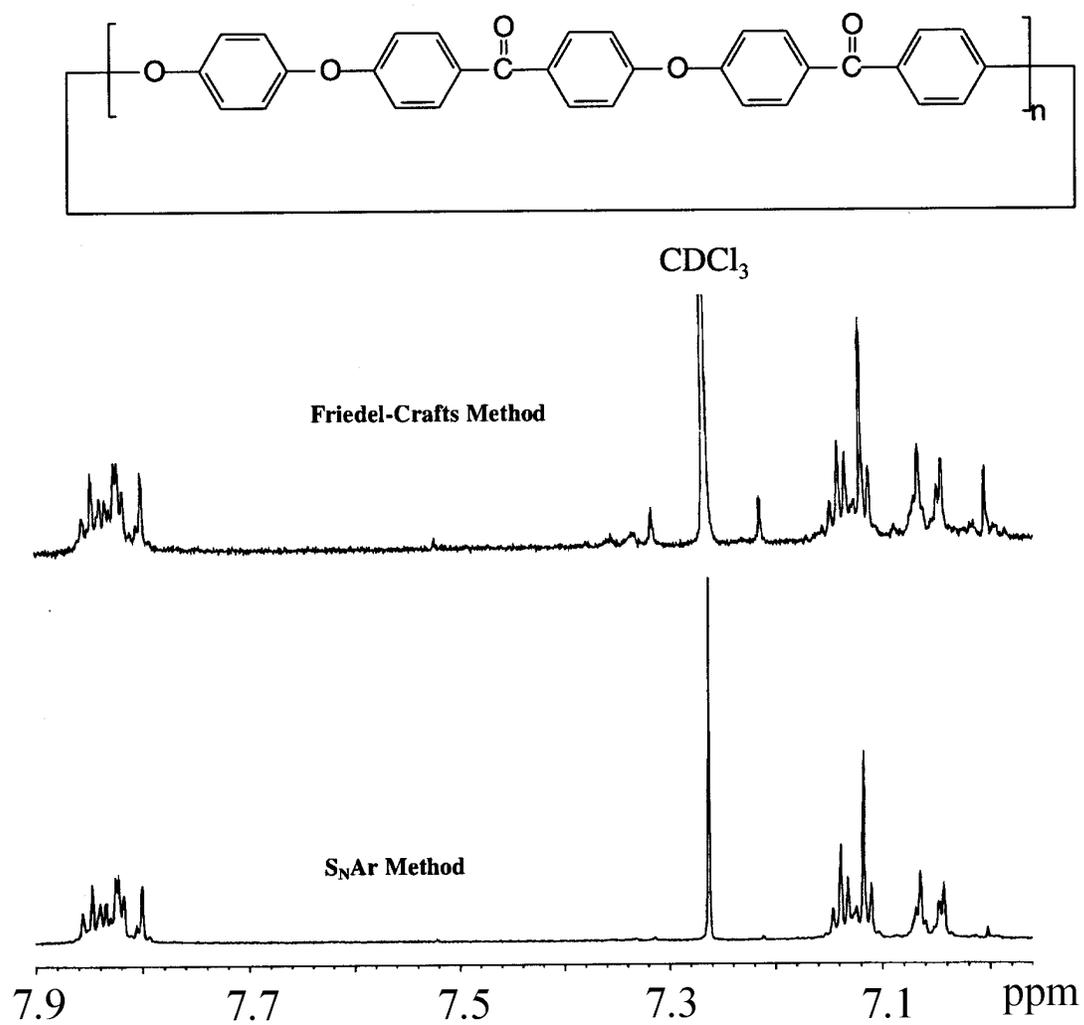


Figure 5.7. 400 MHz ^1H NMR spectra of macrocyclic mixture synthesized from different methods in CDCl_3 .

5.17 was obtained in 10 % yield. It was isolated by exhaustive extraction with chloroform. According to TLC, only the cyclic tetramer was obtained and there was no evidence for formation of the cyclic octamer again, as a result of poor solubility. This macrocycle has very little solubility in chloroform, THF and DMSO, common solvents for this type of macrocycle. The ^1H NMR spectrum of the cyclic tetramer is shown in Figure 5.8. As expected, due to the highly symmetric structure, the spectrum is quite simple. There are only two doublets at 7.83 and 7.12 ppm. There is no evidence of terminal groups. The starting material diacid chloride **5.11** has four doublets and the diphenoxy starting material **5.16** has a characteristic triplet at $\delta=7.42$ ppm.

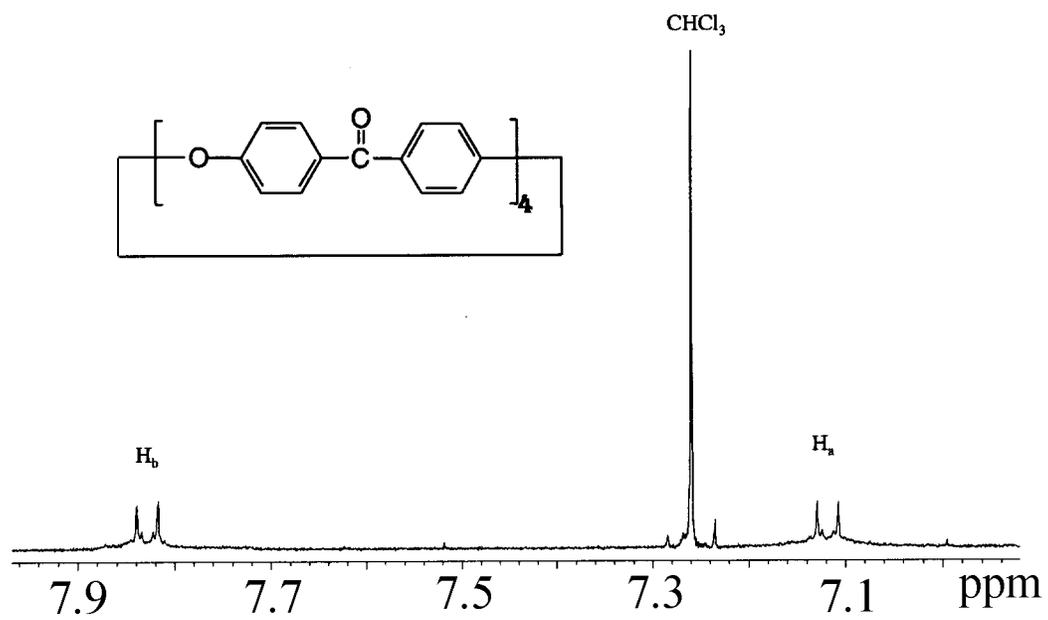


Figure 5.8. 400 MHz ^1H NMR spectrum of macrocycle **5.17** in CDCl_3 .

5.4 Conclusions

It is demonstrated that macrocycles can be synthesized by Friedel-Crafts acylation reaction. However, this reaction is limited by the low solubility of intermediates, hydrolysis and in some cases unknown side reaction. The yield is surprisingly low. Considerable work needs to be done before the reaction is as useful as the nucleophilic aromatic substitution to generate macrocyclic monomers.

5.5 Experimental

Materials

All the materials were used as received. 4-Phenoxyphenol, phenol, 4,4'-difluorobenzophenone and 4, 4'-difluorodiphenyl sulfone were provided by Aldrich. Anhydrous aluminum chloride and DMAc were supplied by Fisher.

Measurements

Melting points were determined on a Haake-Buchler capillary melting point apparatus and were corrected. ^1H and ^{13}C NMR experiments were performed at room temperature on Bruker WP 270 MHz or Varian Unity 400 MHz NMR Spectrometers using tetramethylsilane as the internal standard. The X-ray structure was provided by Dr. Rheingold's group at the University of Delaware.

Synthesis of Ethyl 4-hydroxybenzoate

To a 1L round bottom flask with a magnetic stirrer and a condenser were added ethanol (400 mL, 6.8 mol), 4-hydroxybenzoic acid (40 g, 0.29 mol) and 10 mL concentrated sulfuric acid as catalyst. The reaction was refluxed for about 15 hours. TLC indicated that the reaction was complete. The ethanol solution was poured into 1000 mL 3 % aqueous potassium solution to precipitate the product and remove trace amounts of starting material. A white precipitate was filtered and recrystallized in ethanol. Yield 41.5 g (86 %); mp 116.4-118.2 °C (lit.⁶ mp

[6] Marx, J. N. *J. Amer. Chem. Soc.* **1974**, 96, 2121.

111-112 °C); ¹H NMR (CDCl₃): δ=7.97 (d, J=6 Hz, 2H), 6.90 (d, J=6 Hz, 2H), 4.35 (q, J=7 Hz, 2H), 1.38 (t, J=7 Hz, 3H).

Synthesis of Methyl 4-hydroxybenzoate

This compound was similarly synthesized from methanol and 4-hydroxybenzoic acid. Yield 78 %; mp 123.2-125.2 °C (lit.⁷ mp 127.7-128.3 °C); ¹H NMR (acetone-d₆): δ=9.17 (s, 1H), 7.89 (d, J=6Hz, 2H), 6.92 (d, J=6 Hz, 2H), 3.82 (s, 3H).

Synthesis of 4,4'-diphenoxybenzophenone (5.16)

To a 250 mL round bottom flask equipped with a Dean-Stark trap, a condenser, mechanical stirrer and nitrogen inlet-outlet were added 4,4'-difluorobenzophenone (3.273 g, 15 mmol), phenol (2.82 g, 30 mmol), potassium carbonate (1.518 g, 11.4 mmol), 70 mL toluene and 50 mL DMAc. The reaction was refluxed for 2 hours and then toluene was removed. The reflux was extended for another 22 hours. The product precipitated out during the reaction. The mixture was poured into a large amount of water. The product was filtered, washed with water and dried in a oven. Yield 5.42 g (99 %); mp 145.5-148.1 °C (lit.⁸ mp 145-146 °C); ¹H NMR (CDCl₃): δ=7.79 (d, J=8.8 Hz, 4H), 7.40 (t,

[7] Buehler, G. C. *J. Org. Chem.* **1937**; 167, 174.

[8] Fuson, E. *J. Amer. Chem. Soc.* **1959**, 81, 4858.

J=8.8 Hz, 4H), 7.20 (t, J=8.8 Hz, 2H), 7.09 (d, J=8.8 Hz, 4H), 7.03 (d, J=8.8 Hz, 4H).

Synthesis of Compound 5.6

To a 250 mL one neck flask equipped with a Dean-Stark trap, mechanical stirrer and nitrogen inlet-outlet were added 100 mL DMAc, 100 mL toluene, potassium carbonate (2.49 g, 18 mmol), methyl 4-hydroxybenzoate (5.000g, 32.8 mmol) and 4, 4'-difluorodiphenylsulfone (4.178 g, 16.4 mmol). The reaction was kept for three hours before toluene was removed and then continued for two days. The product was isolated by removing the solvent under vacuum, washing the residue with water and drying in vacuum overnight. Yield 8.4 g (99 %); mp 141.0-145.0 °C (lit.⁹ 136-139 °C); ¹H NMR (270 MHz, d₆-acetone): δ=8.08 (d, 4H), 8.04 (d, 4H), 7.25 (d, 4H), 7.21 (d, 4H), 3.88 (s, 6H).

Synthesis of Compound 5.7

To a 100 mL one neck round bottom flask with a magnetic stirrer and a condenser were added 100 mL 20 % KOH aqueous solution and compound **5.6** (2.57 g, 5 mmol). The reactant gradually dissolved to become a clear homogeneous solution after reflux for 6 hours. The solution was neutralized with 10 % HCl to precipitated out the product. The product was dried in vacuum

[9] Grisle R. A. *MS Thesis*, Virginia Tech, **1992**.

overnight. Yield 2.32 g (95 %); mp 301-303 °C (lit.¹⁰ mp 306-308 °C). ¹H NMR (400 MHz, d₆-acetone): δ=8.11 (d, 4H), 8.04 (d, 4H), 7.26 (d, 4H), 7.21 (d, 4H).

Synthesis of Compound 5.8

To a 100 mL one neck round bottom flask with a magnetic stirrer and a condenser were added 30 mL thionyl chloride, diacid **5.7** (1.724 g, 3.5 mmol) and three drops of DMF. The reaction was refluxed for about 6 hours. Excess thionyl chloride was removed under vacuum to get the product. Crude yield 1.7 g (92 %); mp 184.8-187.0 °C (lit.¹⁰ mp 184-189 °C); ¹H NMR (400 MHz, CDCl₃): δ=8.15 (d, J=9.2 Hz, 4H), 7.99 (d, J=8.8 Hz, 4H), 7.17 (d, J=8.8 Hz, 4H), 7.10 (d, J=9.2 Hz, 4H).

4,4'-Oxybenzoyl chloride (**5.13**) was synthesized under similar conditions and purified by recrystallization in toluene. Yield 81 %; mp 88.3-89.0 °C (lit.¹¹ mp 82-83 °C). ¹H NMR (400 MHz, CDCl₃): δ=8.18 (d, J=9Hz, 4H), 7.15 (d, J=9 Hz, 4H).

Synthesis of Compound 5.9

Compound **5.9** was synthesized under similar conditions for compound **5.6**. The product was isolated by extraction of the crude product with methylene

[10] Idage, S. B.; Idage, B. B.; Shinde, B. M.; Vernekar, S. P. *J. Polym. Sci. Polym. Chem. Ed.* **1989**, *27*, 583.

[11] Partridge, J. P. *J. Pharm. Pharmacol.* **1952**, *4*, 533.

chloride and precipitation in methanol. Yield 58 %; mp 164.8-168.4 °C; ^1H NMR (400 MHz, CDCl_3): δ =8.08 (d, J =8.8 Hz, 4H), 7.93 (d, J =8.8 Hz, 4H), 7.09 (d, J =8.8 Hz, 4H), 7.06 (d, J =8.8 Hz, 4H).

Synthesis of Compound 5.11

To a 500 mL round bottom flask equipped with a condenser and magnetic stirrer were added diester **5.9** (8.00 g, 16 mmol) and 50 mL 20 % aqueous KOH. The mixture was refluxed for three days. The system was neutralized with 10 % HCl and the product was isolated as a solid. Yield 6.9 g (98 %); no melting point was observed; ^1H NMR (400 MHz, d_6 -dmsO): δ =7.99 (d, J =8.8 Hz, 4H), 7.82 (d, J =8.8 Hz, 4H), 7.21 (d, J =8.8 Hz, 4H), 7.18 (d, J =8.8 Hz, 4H).

Synthesis of Compound 5.12.

The synthetic procedures for **5.12** are similar to these for compound **5.8**. Yield 72 %; mp 396 °C (DSC, 10 °C/min); ^1H NMR spectrum (400 MHz, CDCl_3): δ =8.15 (d, J =9.2 Hz, 4H), 7.92 (d, J =8.8 Hz, 4H), 7.20 (d, J =8.8 Hz, 4H), 7.12 (d, J =9.2 Hz, 4H).

Friedel-Crafts Acylation Cyclization (general procedure)

To a 1L round bottom flask with a magnetic stirrer, a condenser with mineral oil seal were added 500 mL dried methylene chloride (distilled over P_2O_5) and anhydrous aluminum chloride. Diacid and diphenoxy precursor (2 mmol) dissolved in 70 mL methylene chloride, were added to the reaction flask over a

period of about 3 hours. The reaction continued overnight and was quenched with concentrated HCl. Solvent was removed under vacuum. The brown solid was extracted with chloroform and the solution was treated with potassium hydroxide to obtain the cyclic mixture.

Chapter 6

Ring-Opening Polymerization of Macrocyclic Monomers

6.1 Introduction—Ring-Opening Polymerization Overview

Ring-opening polymerization is a unique polymerization process, in which a cyclic monomer is opened to generate a linear polymer. It is fundamentally different from a condensation polymerization in that there is no small molecule byproduct during the polymerization. Polymers with a wide variety of functional groups can be produced by ring-opening polymerizations. Examples of industrially important polymers made by ring-opening polymerizations are nylon 6, polysiloxane, polycaprolactone and epoxy resin. Ring-opening polymerization has a unique position in polymer chemistry. Preparation of cyclic monomers, studies of catalysis and mechanisms are active areas of research both in academia and industry. These have been subjects of a number of monographs¹⁻⁴ and reviews.

[1] Ivin, K. J.; Saegusa, T. eds. *Ring-opening Polymerization*, Vols. 1-3. Elsevier, London, **1984**.

[2] Saegusa, T., Ed. *Ring-opening Polymerization*, ACS Symposium Series Vol. 59, American Chemical Society, Washington D. C. **1977**.

[3] McGrath, J. E., Ed. *Ring-opening Polymerization: Kinetics, Mechanism, and Synthesis*. American Chemical Society, Washington D. C., **1985**.

A. Polymerizability of Cyclic Compounds

The thermodynamic polymerizability of a cyclic monomer has been elegantly summarized by Ivin.⁵ Negative free energy change from monomer to polymer is the thermodynamic driving force for the ring-opening .

$$\Delta G = \Delta H - T\Delta S$$

For small sized cyclic compounds, the enthalpy term is negative and dominant. The strains in bond angles and bond lengths are released upon ring-opening. Such monomers can be almost completely converted to polymers. For medium sized cyclic monomers (5-7membered rings), the ring strain is small and the entropy is a small positive term. Thus, the overall driving force (ΔG) is small and the extent of polymerization is little or no reaction. For 8-, 9- and 10-membered monomers, the enthalpy term is dominant and negative, while the $T\Delta S$ term is relatively small. The strain is due to the non-bonded interactions between atoms. Essentially complete conversion to polymer is possible. When the ring size is very large and there is virtually no ring-strain ($\Delta H \cong 0$), the driving force for ring-opening polymerization is the large increase of entropy. The polymerization should be an athermal process.

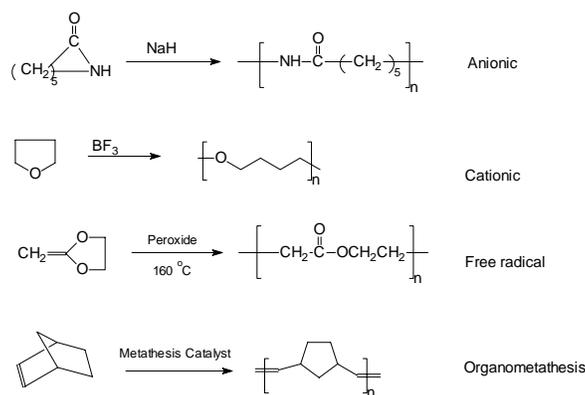
[4] Brunelle, D. J., Ed. *Ring-opening Polymerization: Mechanisms, Catalysis, Structure, Utility*, Carl Hanser Verlag, NY, **1993**.

[5] Ivin, K, J. *Makromol. Chem. Macromol. Symp.* **1991**, 42/43, 1.

B. Mechanisms of Ring-opening Polymerization

In addition to the thermodynamic criterion, there must be a kinetic pathway for the ring to open and undergo the polymerization reaction. Therefore, the kinetics of the ring-opening of the monomer should also be considered. A variety of mechanisms operate for ring-opening polymerizations, including anionic, cationic, metathesis and free radical mechanisms. Examples of various ring-opening polymerizations are shown in Scheme 6.1.

Scheme 6.1



In contrast to the great interest in the ring-opening polymerization of macrocyclic monomers to generate poly(ether ketone)s and poly(ether sulfone)s, there has been no detailed ring-opening polymerization study of this type of monomers. The ring-opening polymerization of macrocyclic poly(ether ketone)s or sulfones was only slightly covered in early works. The only more detailed study came from Hay's group.⁶ In this chapter, the ring-opening polymerization of the macrocyclic monomers prepared in previous chapters is addressed.

[6] Wang, Y-F; Chan, K. P.; Hay, A. S. *J. Polym. Sci.: Part A: Polym. Chem.*

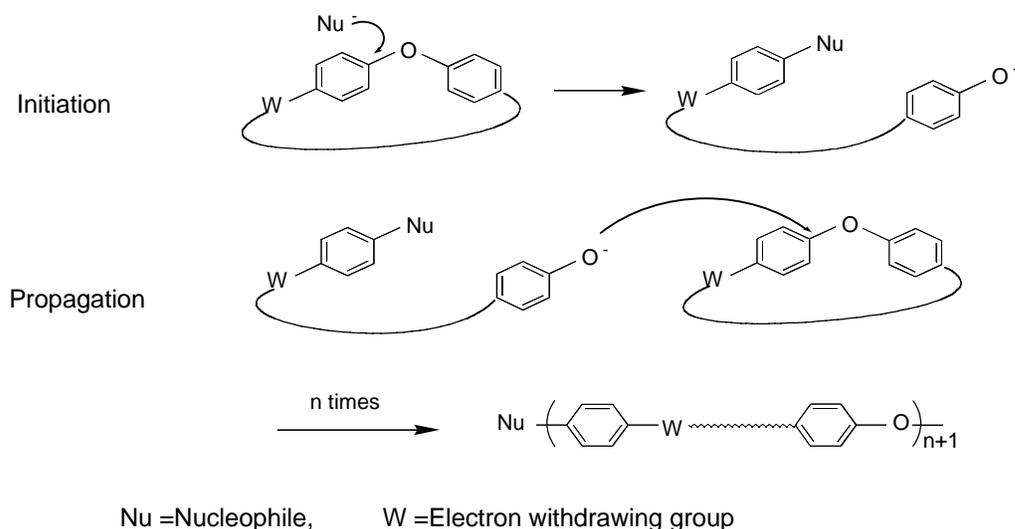
1996, 34, 375.

6.2 General Considerations of the Ring-opening Polymerizations of Macrocyclic Monomers.

A. Mechanism of Ring-opening Polymerization

The ring-opening polymerization of cyclic poly(ether ketone)s or sulfones takes advantage of the ether exchange reaction as pointed out in the pioneering work of Colquhoun and coworkers.⁷ The mechanism for the ring-opening is generalized in Scheme 6.2. The ether linkage, which is activated by the electron withdrawing group, is broken by nucleophilic attack to generate the phenoxide. The phenoxide opens the cyclic monomer successively to form the linear polymer.

Scheme 6.2



[7] Colquhoun, H. M.; Dudman, C. C.; Thomas, M.; O'Mahoney, C. A.; Williams, D. J. *J. Chem. Soc., Chem. Commun.* **1990**, 336.

B. Dispersion of Initiator and Preparation of Sample

As indicated by the mechanism, a nucleophilic initiator is necessary for the ring-opening polymerization. The ideal case would be a homogeneous dispersion of an initiator in the cyclic mixture. In our early study, it was found that the initiator can be mechanically mixed with the cyclics to initiate the ring-opening polymerization. However, the dispersion may not have been even, since the amount of the initiator was very small. Another problem was the stability of the metallic phenoxides-the typical initiators, which are not stable in the solid state. After a few days, they became purple colored indicating some oxidation. Therefore, the solution mixing of an initiator with monomer was preferred. Ethanol was a good solvent for the metallic phenoxides and other initiators such as CsF and Na₂S. The ethanol solutions of the initiators appeared to be stable. Precautions were made about the shelf time of the initiator (less than two weeks). The CsF solution in ethanol was quite stable and there was no decrease in its reactivity within about 8 months. The ethanol solution of the an initiator was mixed with the chloroform solution of the macrocyclic monomer and no precipitate was observed during the mixing probably, because the precipitate had too small a particle size to be visually observed. The solution was evaporated under vacuum to give a homogeneous mixture of the macrocycle. Care must be taken to dry the sample thoroughly before the ring-opening polymerization. In our early study, the sample was dried under low vacuum and inconsistent results were obtained. Sometimes the sample could not be polymerized. Later on it was found this was due to a small amount of water or

solvent (ethanol), which may act as chain transfer agent. Drying the sample at 120 °C under a vacuum of better than 10^{-4} torr overnight was sufficient. As indicated by the mechanism, the active species of the growing chain is the phenoxide, which can be oxidized very easily at high temperatures (>300 °C) if a small amount of oxygen is present. Inconsistent results were obtained under nitrogen protection or low vacuum. Therefore, all the polymerizations were carried out on a vacuum line with vacuum of approximately 10^{-5} torr. The oxygen level was estimated to be as low as 3 ppm. However, under such a high vacuum the small sized macrocycle sublimed at the polymerization temperature. It was found under a static vacuum the evaporation of monomer can be ignored.

C. Monitoring the Polymerization Process

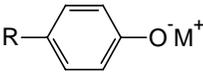
The polymerization process was monitored by four techniques: Gel Permeation Chromatography (GPC), DSC, rheometry and NMR spectroscopy. The bisphenol-A based macrocyclic monomers and the corresponding polymers were soluble in THF and the progress of the polymerization was conveniently monitored by GPC. By measuring the percentage of high molecular weight fraction and the gel fraction, the total conversion was calculated. DSC measurements were taken to find the thermal transitions of the cyclics and resulting polymer. The polymerizability was visually observed also. If the ring-opening polymerization was incomplete (<95 %) or the initiator was ineffective, the resulting sample remained a powder and had poor mechanical properties. If the polymerization was nearly complete, a tough and flexible polymer was usually obtained. Sometimes there were changes in the chemical shifts of the

macrocycle protons compared with those of the polymers. Therefore, the ring-opening polymerization could be monitored by NMR. Rheometry was a very effective tool to monitor the progress of ring-opening polymerization by measuring the change in viscosity as a function of reaction time.

6.3 Polymerization Results and Discussion

Selection of an appropriate initiator was the first objective. The initiators tried are listed in Table 6.1.

Table 6.1 Initiators for Ring-opening Polymerization

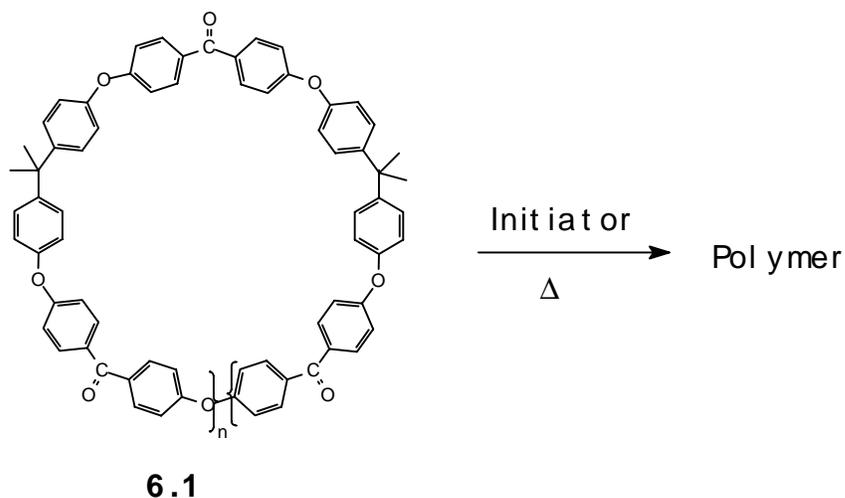
Entry	Initiator	Effectiveness
1	Ph_3P	No
2	$\text{Ph}_4\text{P}^+\text{Cl}^-$	No
3	$\text{Ph}_3\text{P}^+\text{EtBr}^-$	No
4	Ph_4POH	No
5	NaF	No
6	KF	No
7	CsF	yes
8	Na_2S	yes
9	 $\text{R}-\text{C}_6\text{H}_4-\text{O}^-\text{M}^+$ $\text{M}=\text{Li}, \text{Na}, \text{K}, \text{Cs}$	yes

The phosphonium salts (entries 2-4) are not good initiators for the ring-opening polymerization. The purpose of selecting the bulky phosphonium counter ion was to protect the active phenoxide intermediate in an attempt to establish a living polymerization. After heating a cyclic poly(ether ether ketone) monomer with 5 mol % of the initiator at 340 °C for an hour, there was no indication of polymerization by DSC or visual observation. This suggested that the chloride and bromide ions were not sufficiently nucleophilic for the exchange reaction. The neutral triphenyl phosphine was not an initiator either. Among the metallic fluoride category (entries 5-7), the sodium and potassium fluorides were not effective initiators, but cesium fluoride was an excellent initiator. Probably the sodium and potassium fluorides were in the tight ion state and thus were not effective. Another good type of initiator was the metallic phenoxide family. The metal ions can be lithium, sodium, potassium and cesium. Polymerization initiated by lithium phenoxide was much slower. Sodium sulfide was proven to be a good initiator.

Polymerization temperature was another parameter to be considered. Although there was a report⁸ of polymerization carried out as low as 275 °C, the polymerization temperature is limited by the melting point of the cyclic mixtures and, in the case of semicrystalline polymer, by the crystallization temperature of the polymer. Generally, the polymerization was carried out above 300 °C.

[8] Teasley, M. F.; Harlow, R. L. Wu, D. Q. *Am. Chem. Soc. Div. Polym. Chem. Polym. Prepr.* **1997**, 38(1), 125.

Scheme 6.3



Macrocyclic mixture **6.1** has a melting point of 320 °C. The cyclic nature of this monomer was established by ¹H NMR and MALDI-TOF-MS. Its polymerization was more systematically studied to establish general polymerization conditions (Scheme 6.3).

The monomer was first polymerized with 1-4 mol % CsF at 350 °C. The polymerization results are listed in Tables 6.2-6.4. The molecular weights listed are for the soluble fraction only. Percent of polymer refers to the amount of polymer in the soluble fraction as calculated from GPC.

Table 6.2. Polymerization results for macrocyclic mixture **6.1** with 1 mol % CsF at 350 °C

time (min)	gel (%)	polymer (%)	conversion (%)	M _n	M _w
30	0	30	30	14k	24 k
60	0	32	32	16 k	49 k
90	0	33	33	16 k	56 k

Table 6.3. Polymerization results for macrocyclic mixture **6.1** with 2 mol % CsF at 350 °C

time (min)	gel (%)	polymer (%)	conversion (%)	M _n	M _w
2	0	35	35	21 k	51 k
5	0	45	45	30 k	164 k
10	12	48	54	28 k	79 k
30	76	58	91	21 k	40 k

Table 6.4. Polymerization results for macrocyclic mixture **6.1** with 4 mol % CsF at 350 °C

time (min)	gel (%)	polymer (%)	conversion (%)	M _n	M _w
2	0	47	47	28 k	204k
10	63	57	84	22 k	45 k
30	84	87	98	18 k	38 k

With only 1 mol % (0.15 wt %) CsF added as the initiator, the polymerization was slow. After 90 minutes of reaction, the conversion was only 33 %. The molecular weight did not change much with time. When 2 mol % CsF was used, the conversion was pushed to 91 % after 30 minutes of reaction with 76 % gel. The molecular weight increased with reaction time at first, reaching the highest point at about 5 minutes (M_n=30 k) and the molecular weight distribution was very broad (PDI=5.5), which was due to the very high molecular weight fraction. Then the molecular weight decreased while the reaction continued and interestingly, the molecular weight distribution reached the equilibrium value (2.0) predicted for a polycondensation polymer.

When 4 mol % CsF was used, the molecular weight reached the highest point at 2 minutes because the reaction was faster. The molecular weight distribution was very broad (PDI=7.2) at this stage. Again the molecular weight decreased with increasing reaction time. After 30 minutes of reaction, the conversion was nearly complete (98 %) with 84 % gel. The number average molecular weight was 18 k and the weight average weight was 38k; these values are virtually the same as those when 2 mol % CsF was used. The monomer left was predominantly the cyclic monomer as can be seen in Figure 6.1. It is obvious that when more initiator was used, the polymerization rate was increased (Figure 6.2).

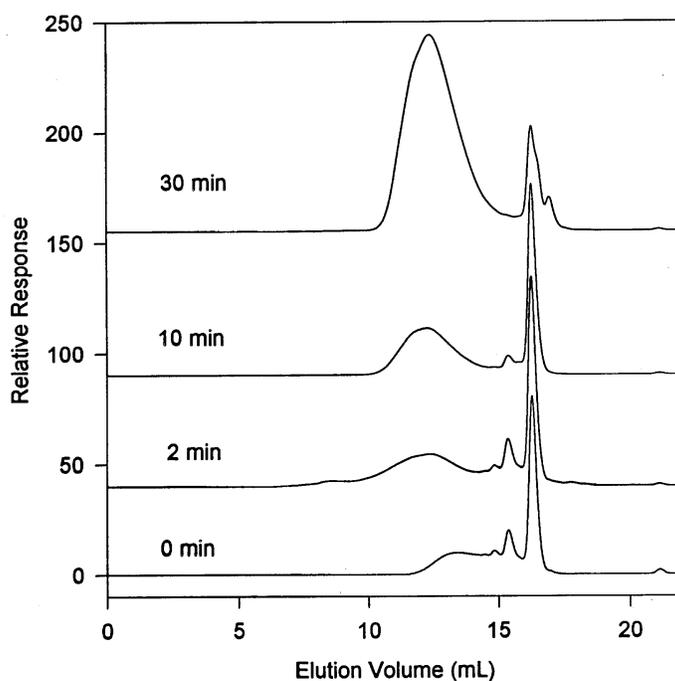


Figure 6.1. GPC chromatograms of soluble fraction of polymerized samples of macrocyclic monomer **6.1** with 4 mol % CsF at 350 °C.

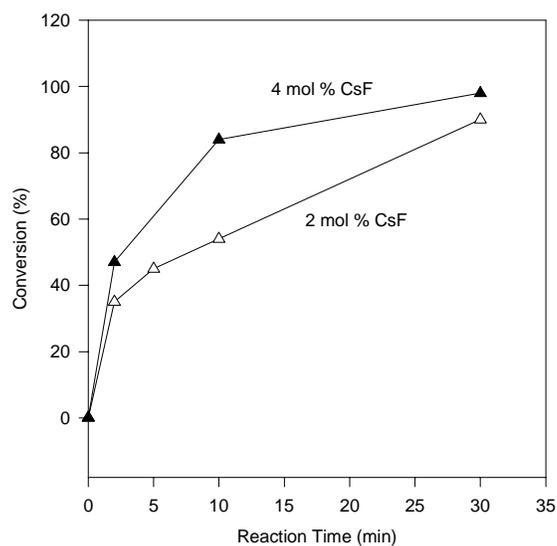


Figure 6.2. Conversion of macrocyclic monomer **6.1** to polymer with different amounts of CsF at 350 °C.

Table 6.5. Polymerization results for macrocyclic monomer **6.1** with 4 mol % CsF at 330 °C

time (min)	gel (%)	polymer (%)	conversion (%)	M _n	M _w
2	0	39	39	24k	64k
5	0	49	49	28k	133k
30	33	49	66	25k	56k
90	92	71	98	13k	25k

Table 6.6. Polymerization results for macrocyclic mixture **6.1** with 4 mol % CsF at 370 °C

time (min)	gel (%)	polymer (%)	conversion (%)	M _n	M _w
2	0	47	47	29	120
30	94	66	98	18	30

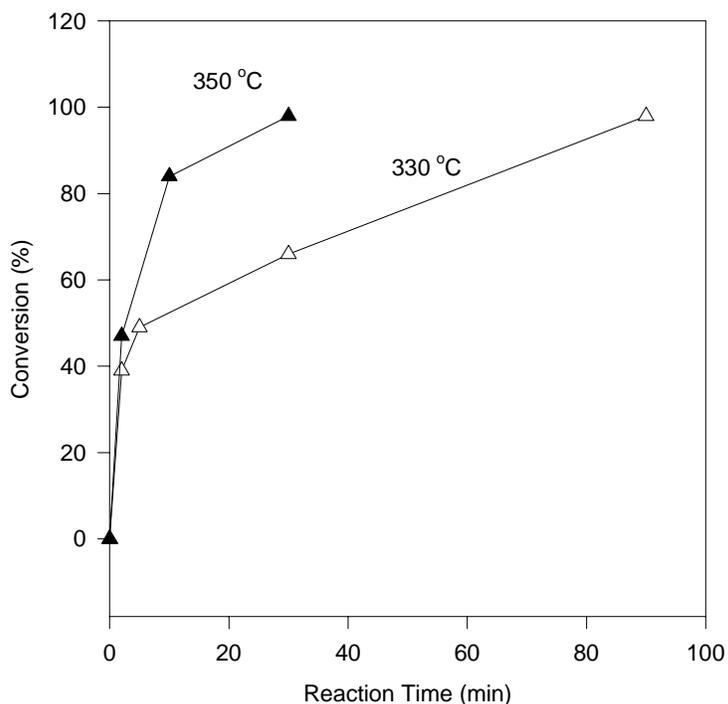


Figure 6.3. Conversion of macrocyclic monomer **6.1** to polymer at two different temperatures with 4 mol % CsF.

With the same amount of initiator (4 mol % CsF), the polymerization was carried out at two different temperatures (330 °C and 370 °C). At 330 °C, The polymerization rate was quite low. The conversion after half an hour was only 66 %. It took about 90 minutes to get a conversion of 98 %, but the molecular weight was slightly lower than in the higher temperature cases (350, 370 °C). Figure 6.3 clearly indicates that the polymerization rate was increased when the polymerization was carried out at higher temperature, but the molecular weight of the soluble fraction did not change much.

The same macrocycle was polymerized with 2 and 4 mol % potassium phenoxide of bisphenol-A at 350 °C. Results (Table 6.7-6.8) were similar to those obtained when CsF was used.

Table 6.7 Polymerization results for macrocyclic mixture **6.1** with 2 mol % potassium phenoxide of bisphenol-A at 350 °C

Time (min)	gel %	polymer %	conversion %	M _n	M _w
2	31	49	65	27k	68k
10	59	55	81	26 k	51k
30	95	72	99	17k	28k
60	98	76	99	13k	21k

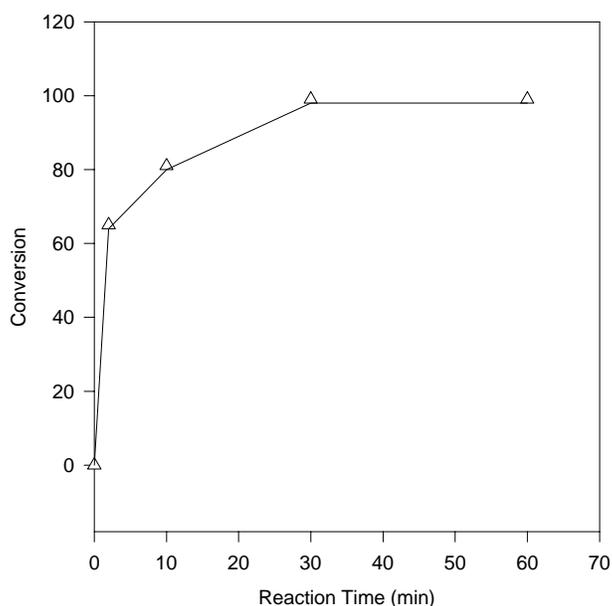


Figure 6.4. Conversion of macrocyclic monomer **6.1** to polymer with 2 mol % potassium phenoxide of bisphenol-A

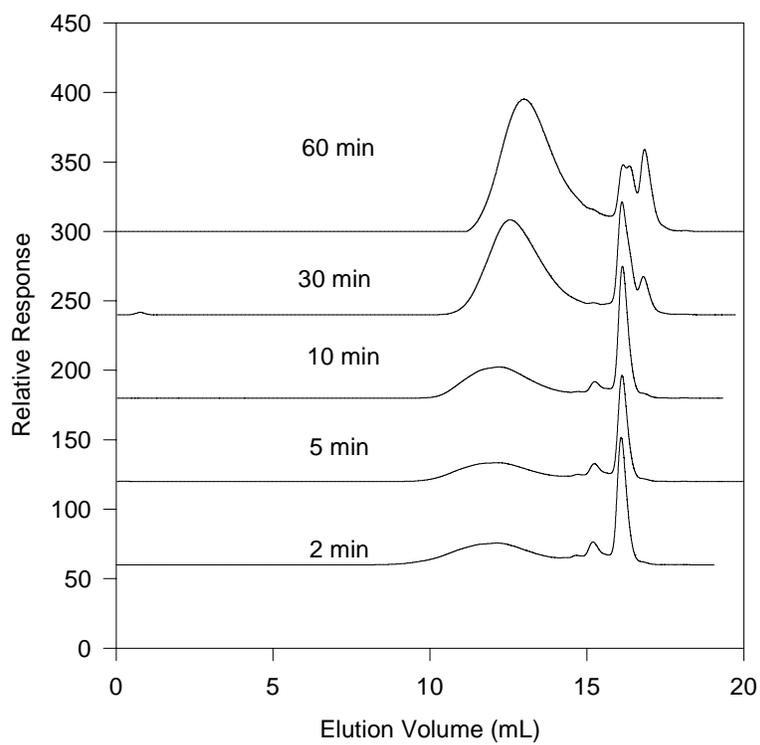


Figure 6.5. GPC chromatograms of soluble fractions of polymerized samples of macrocyclic monomer **6.1** with 2 mol % potassium phenoxide of bisphenol-A at 350 °C.

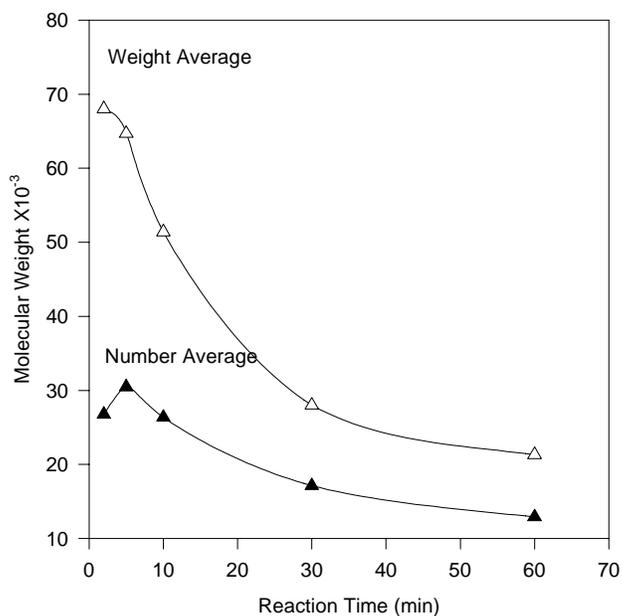


Figure 6.6. Molecular weight change of polymerized samples of macrocyclic monomer **6.1** with reaction time with 2 mol % potassium phenoxide of bisphenol-A

Table 6.8. Polymerization results for macrocyclic mixture **6.1** with 4 mol % potassium phenoxide of bisphenol-A at 350 °C.

Time (min)	gel %	soluble %	Conversion %	M _n	M _w
2	0	57 %	57	30k	118k
5	53	59 %	81	21	43
10	69	67 %	90	21	38
30	88	78 %	97	15	28

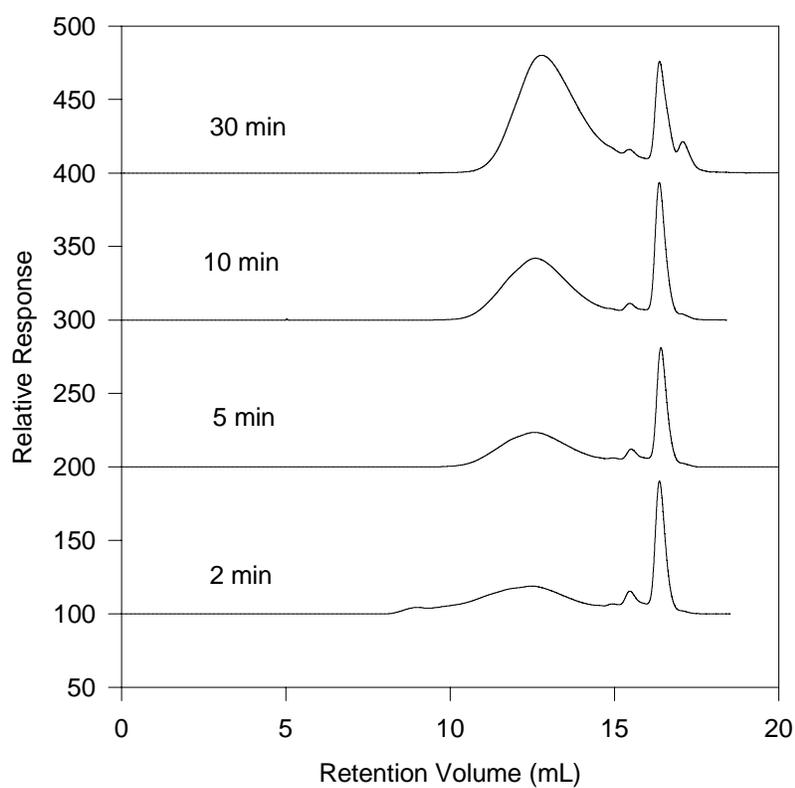


Figure 6.7. GPC chromatograms of soluble fractions of polymerized samples of macrocyclic monomer **6.1** with 4 mol % potassium phenoxide of bisphenol-A at 350 °C.

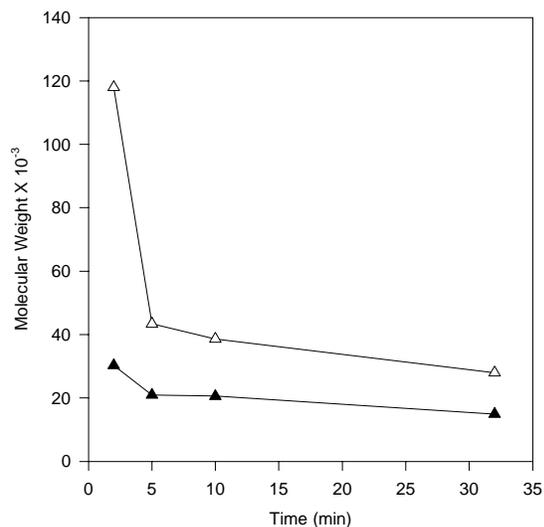


Figure 6.8. Molecular weight change soluble fraction of polymerized samples of macrocyclic monomer **6.1** with reaction time with 4 mol % potassium phenoxide of bisphenol-A

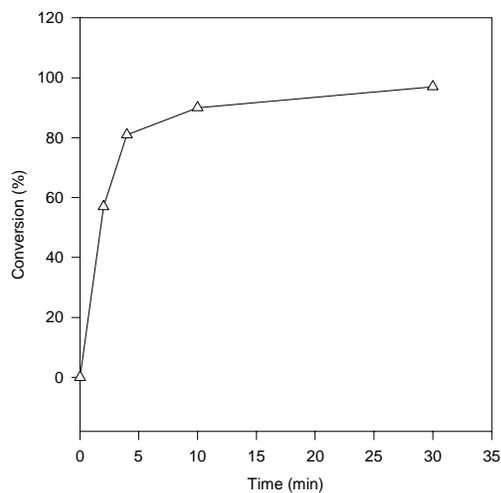


Figure 6.9. Conversion of macrocyclic monomer **6.1** to polymer with 4 mol % potassium phenoxide of bisphenol-A at 350 °C.

When 2 mol % initiator was used, the polymerization was essentially complete within 30 minutes and the polymer was almost completely gelled (95 % gel fraction). The molecule weight of the soluble fraction decreased as the polymerization continued.

When 4 mol % initiator was used, extremely high molecular weight polymer was generated after polymerization for 2 minutes as evident by the presence of the small peak that eluted first in GPC chromatogram (Figure 6.7). The number molecular weight was 30 k and the molecular distribution was quite high (PDI=3.9) with weight average molecular weight of 118 K. The broad distribution was due to the extremely high molecular fraction. As the polymerization time increased, the molecular weight distribution became narrower. The same mixture was polymerized at 390 °C for only 5 minutes. The conversion was 97 %, essentially a complete conversion.

The same macrocycle was polymerized with 4 mol % sodium sulfide. Again a similar trend was observed (Table 6.9, Figures 6.10-12) as above .

Table 6.9. Polymerization results for macrocyclic mixture **6.1** with 4 mol % Na₂S at 350 °C

Time (min)	gel %	Polymer (%)	Conversion (%)	M _n	M _w
2	0	40	40	23k	48k
5	14	45	53	29k	72k
10	30	40	58	25k	50k
30	83	54	91	19	32k

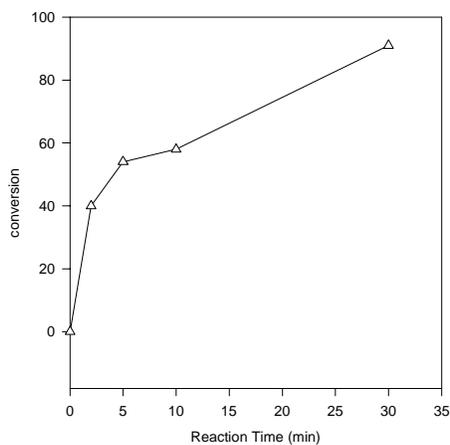


Figure 6.10. Conversion of macrocyclic monomer **6.1** to polymer with 4 mol % potassium salt of bisphenol-A at 350 °C.

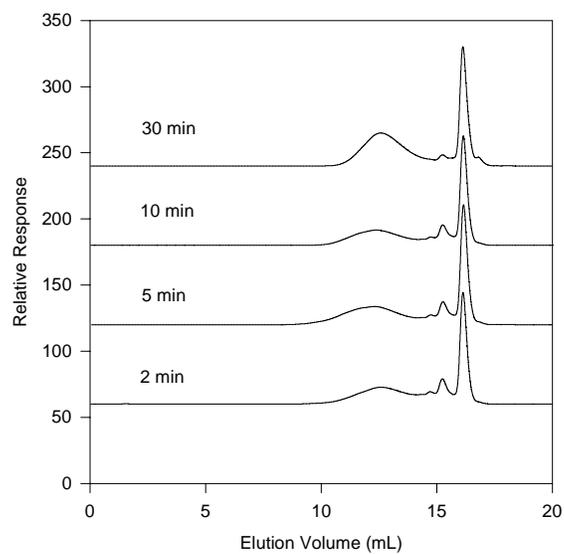


Figure 6.11. GPC chromatograms of soluble fractions of polymerized samples of macrocyclic monomer **6.1** with 4 mol % sodium sulfide at 350 °C.

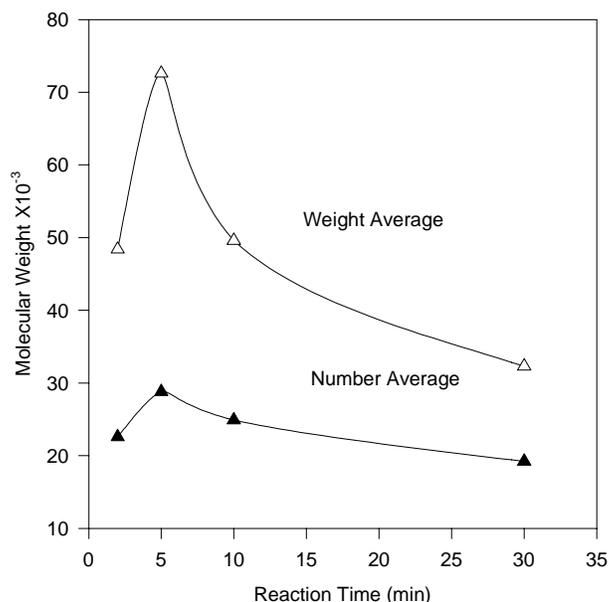


Figure 6.12. Molecular weight change of polymerized samples of macrocyclic monomer **6.1** with reaction time with 4 mol % Na₂S.

Again, the molecular weight decreased with increasing reaction time and its distribution became narrower. The molecular weight did not change much in the late stage of the reaction. The polymerization rate using sodium sulfide as the initiator was much slower than with potassium phenoxide and slower than when CsF was the initiator. This is probably because the counter ion is sodium, which decreases the reactivity of the phenoxide. After 30 minutes of reaction, the conversion was 91 %.

The polymerization (Scheme 6.4) results for macrocyclic monomer **6.2** with 2 mol % CsF are listed in Table 6.10.

Scheme 6.4

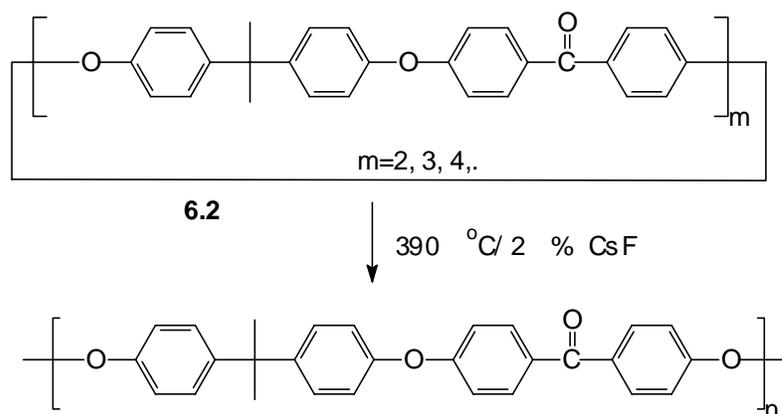


Table 6.10. Polymerization results for macrocyclic monomer **6.2** with 2 mol % CsF at 390 °C.

time (min)	gel (%)	polymer (%)	conversion (%)	M_n	M_w
10	55	95	98	14 k	31k
20	86	94	99	13k	27k
30	88	87	99	11k	21k

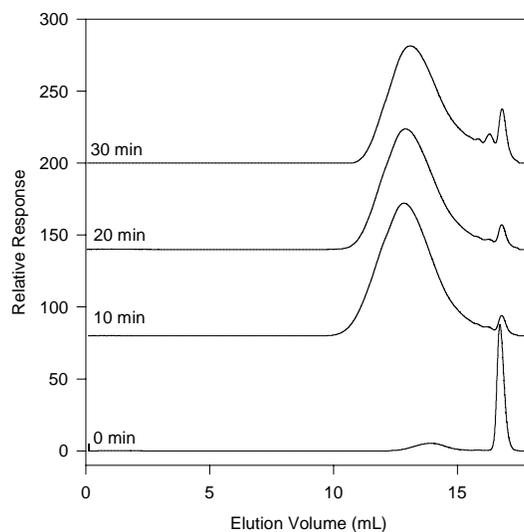


Figure 6.13. GPC chromatograms of soluble fraction of polymerized samples of macrocyclic monomer **6.2** with 2 mol % CsF at 390 °C.

The cyclic mixture was obtained from a four-step synthetic method. It has a melting point of 379 °C. The polymerization was carried out at 390 °C. At such a high temperature, polymerization was essentially complete within 10 minutes. Again the molecular weight decreased with increasing polymerization time, but not very much. The molecular weights had a polydispersity of 2.0, which was close to the theoretically predicted value due to fast chain exchange reaction. Interestingly, the amount of cyclic dimer in the unpolymerized fraction increased as the reaction time was extended. This was probably due to the ring-chain equilibrium.

Results obtained from the polymerization with different initiators, various amounts of initiator and different polymerization temperatures point to the same trend. First, the molecular weight of the soluble fraction near complete conversion does not change very much with the polymerization temperature, or the amount of initiator used. The polydispersity is close to 2.0 also. It is obvious that crosslinking was an inherent phenomenon of the polymerization. Its mechanism was not clear. It appears that when the molecular weight reached a certain level or branching point, the polymer was gelled or crosslinked. This explains why the molecular weight does not change at the late stage of polymerization reaction. At the initial stage the molecular weight was higher and broader. This was probably because the initiator was in a discrete phase and it was necessary for the initiator to diffuse into the cyclic melt to initiate the ring-opening polymerization. The amount of initiator in the cyclic melt was very small and thus the molecular weight was higher. The high molecular weight fraction was either crosslinked or broken down due to the chain-chain exchange reaction. Thus, the molecular weight decreased with increasing reaction time. Nearly complete conversion from monomer to polymer was possible, but the polymer obtained was predominantly crosslinked. The conversion was limited by the thermodynamic ring-chain equilibrium.

The polymerization conditions established from the bisphenol-A based cyclic systems can be applied to the more valuable fully aromatic systems. Unfortunately since these systems are characterized by good solvent resistance and their ring-opening polymerization can not be readily studied by the GPC

experiments. Therefore, DSC was used to monitor the ring-opening polymerization.

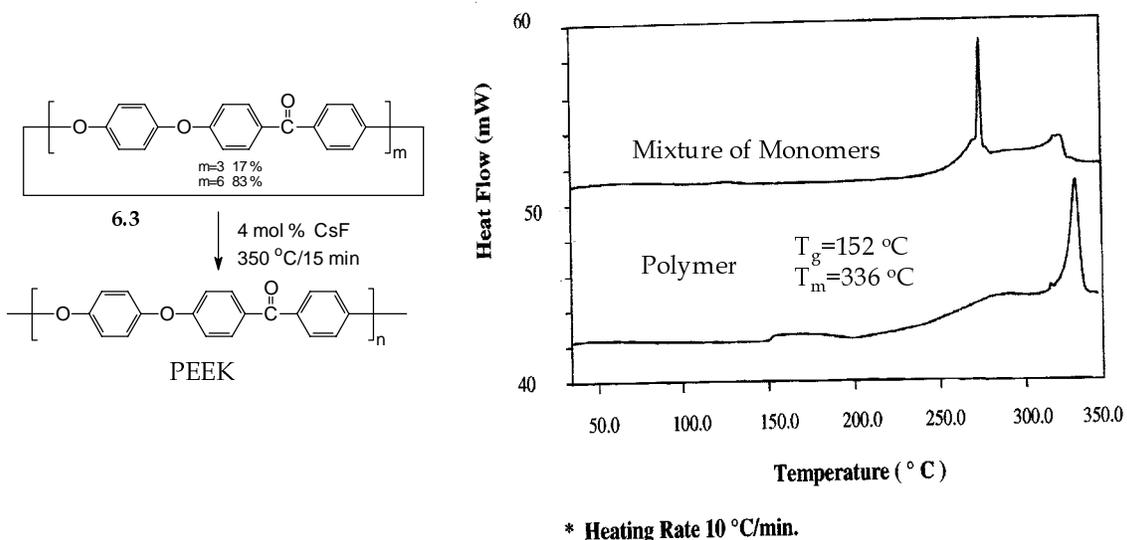


Figure 6.14. DSC thermograms of macrocyclic monomer **6.3** and its polymerized sample.

The polymerization of the macrocyclic mixture consisting of a cyclic trimer and hexamer was polymerized with 4 mol % CsF for 15 minutes at 350 °C (Figure 6.14). A tough and flexible polymer was obtained. The DSC thermogram indicated that it had a glass transition temperature of 152 °C and melting point of 336 °C. These transition temperatures are typical of semicrystalline poly(ether ether ketone). The resulting semicrystalline polymer was only partially soluble in concentrated sulfuric acid, indicating the polymer was somewhat crosslinked. The same mixture was polymerized with 5 mol %

lithium salt of bisphenol-A with the hope that a lithium counter ion would decrease the reactivity of the phenoxide thus avoiding crosslinking problems. The reaction was indeed very slow. After half an hour, the resulting polymer was a powder, indicating no high molecular weight polymer was built up. However, after one hour, a tough and flexible polymer was obtained, which showed a glass transition temperature at 154 °C, a melting point at 332 °C and about 27 % crystallinity. The sample was annealed at 280 °C for half an hour and a sub-melting peak at 279 °C was observed, which is characteristic of PEEK.

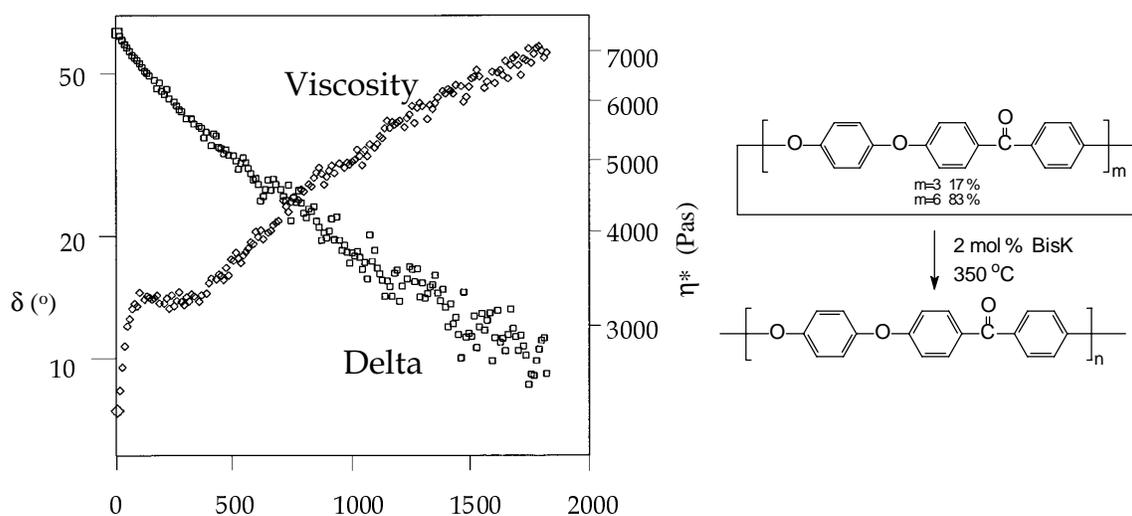


Figure 6.15. Polymerization of macrocyclic monomer **6.3** as monitored by rheometry.

The polymerization of the same cyclic monomer for PEEK at 350 °C with 2 mol % potassium phenoxide was monitored by rheometry. As seen from Figure 6.15, the viscosity increased very rapidly during the initial stage of the

reaction. The viscosity reached 3000 Pa.s within about 5 minutes. The viscosity did not change much after about 3 minutes. Then after 8 minutes it continued to increase with reaction time, reaching about 7000 Pa.s within about half an hour. At the same time the stress-strain phase angle continued to decrease with reaction time. This is an indication that the resulting polymer was more elastic than viscous like suggesting crosslinking of the resulting polymer. In the same polymerization mixture, an equivalent of monofluoroketone endcapping reagent was used and there was no polymerization; there was no change in viscosity.

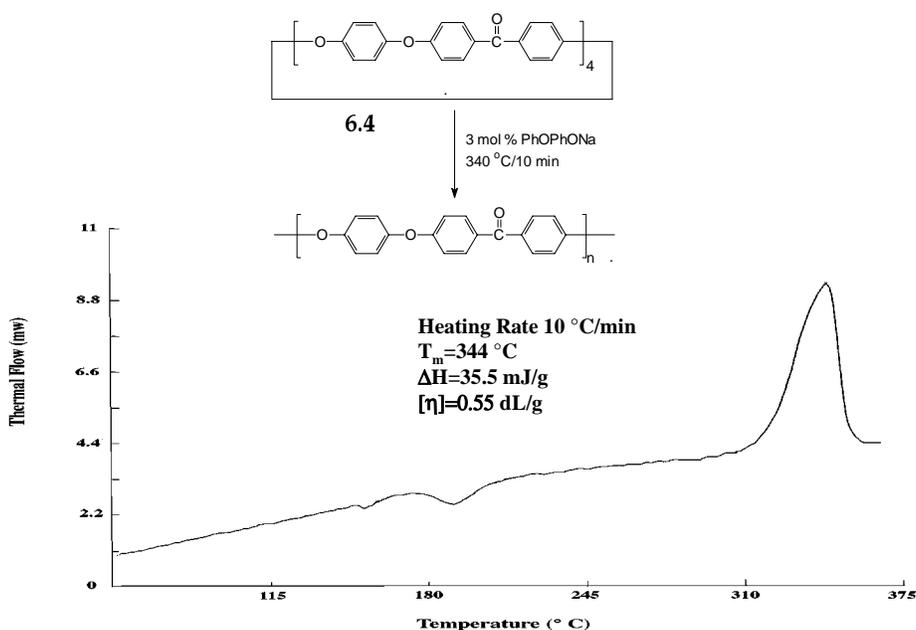
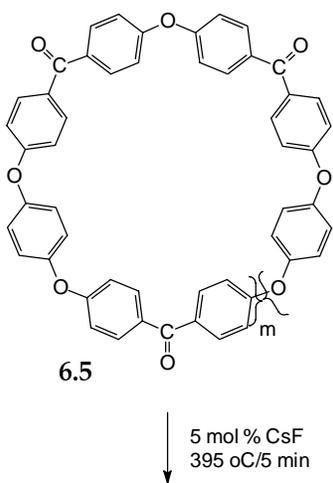


Figure 6.16. DSC thermogram of polymer obtained by ring-opening polymerization of macrocyclic monomer **6.4** .

The polymerization of the 60-membered macrocyclic monomer (**6.4**) for PEEK was carried out with 3 mol % sodium 4-phenoxyphenoxide at 340 °C for

10 minutes. The resulting polymer was almost completely soluble. It was flexible and tough and had an inherent viscosity of 0.55 dL/g. In the first curve of the DSC thermograms of the polymerized sample, no T_g was observed. It had a crystallization temperature around 192 °C and a melting point at 344 °C. In the second heating curve, a T_g was observed at 159 °C and the melting point was decreased to 338 °C; the melting enthalpy was 43J/g, corresponding to a PEEK crystallinity of 33%. After the DSC experiment the polymer was hard and was only partially soluble in concentrated sulfuric acid, indicating further crosslinking upon heating in the DSC pan.



Polymer

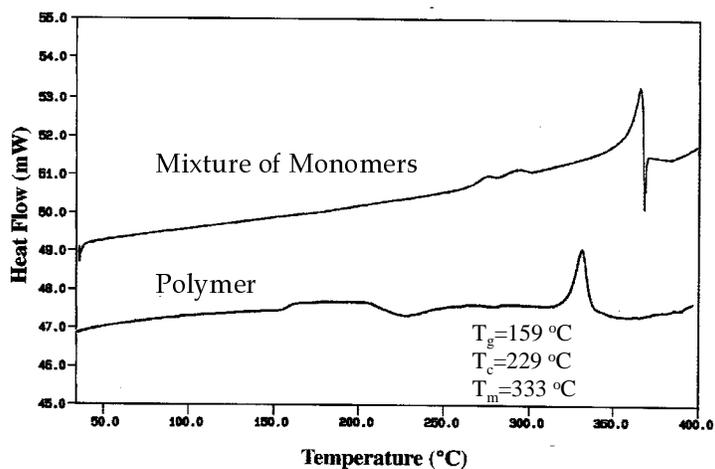


Figure 6.17. DSC thermograms of macrocyclic monomer **6.5** and its polymerized sample.

The polymerization of the all aromatic macrocycle **6.5** consisting of two EEK and one EK repeat units was carried out with 5 mol % CsF at 395 °C for five minutes (Figure 6.17). The macrocyclic mixture had a melting point of 365

°C. There was no T_g observed for the neat cyclic sample. However, the resulting semicrystalline polymer showed a T_g at 159 °C, a crystallization peak at 229 °C and a melting point peak at 333 °C. Again the polymer was only partially soluble in sulfuric acid, indicating the polymer was somewhat crosslinked. The polymer was tough and flexible. It should be pointed out that the polymer was very probably a random copolymer due to the chain-chain exchange reaction, but it was still crystalline. This is not surprising because the ether and ketone groups are crystallographically equivalent.

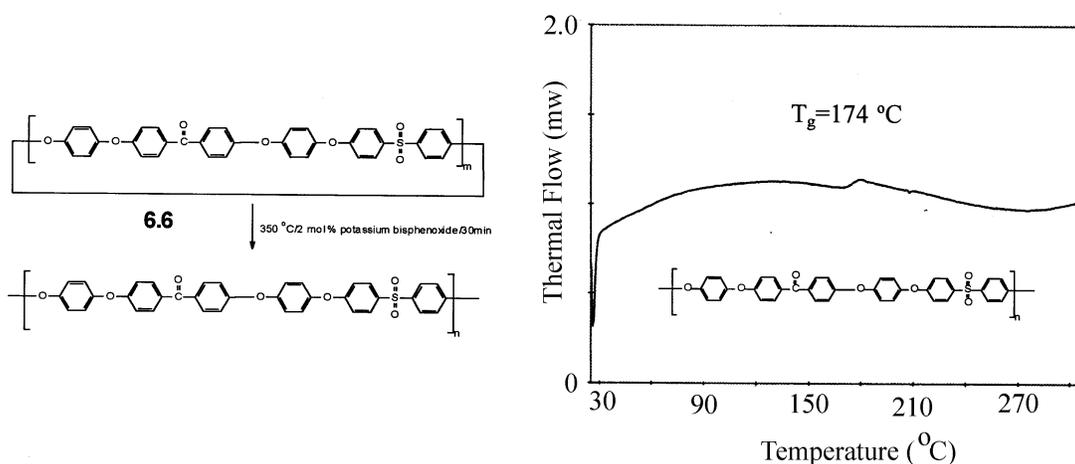


Figure 6.18. DSC thermogram of polymer obtained after polymerization of macrocyclic monomer **6.6**.

The all aromatic comacrocyclic (**6.6**) containing EEK and EES repeat units was polymerized with 2 mol % bisphenoxide at 350 °C for 2, 5, 15, and 30 minutes. After 30 minutes of reaction, a tough flexible polymer was obtained. Before that the polymer was brittle, indicating insufficient conversion. The

polymer was amorphous and had a T_g of 174 °C (Figure 6.18), lower than predicted (179 °C) by the Fox equation because of a small amount of unpolymerized cyclics, which served as plasticizer. In contrast the monomer had a melting point at 301 °C. The resulting polymer is probably a random copolymer because the chain-chain exchange rate should be almost the same as the propagation rate.

6. 4 Conclusions

After a more detailed study of the ring-opening polymerization conditions; the following conclusion can be drawn.

1. CsF, lithium, sodium and potassium phenoxides and sodium sulfide were effective ring-opening polymerization initiators.
2. The crosslinking reaction was an inherent phenomenon which can not be avoided at this time.
3. Due to the crosslinking side reaction, the molecular weight of the soluble fraction near complete conversion did not change very much with the amount of initiator, the polymerization temperature or the initiator. During polymerization, the high molecular weight of the soluble fraction decreased with reaction time and distribution was close to PDI=2.0 for the final polymer.
4. Under the typical polymerization conditions (350 °C, 30 minutes, 2-4 mol % initiator), the conversion of the monomer to polymer was nearly complete.
5. It was demonstrated for the first time that semicrystalline poly(ether ketone)s can be obtained by the using macrocyclic monomer techniques. Particularly, the important PEEK was produced through ring-opening polymerization of macrocyclic monomers.

6.5 Experimental

Materials: Macrocyclic monomers used for the polymerization study were reported in previous chapters. Bisphenol-A was purified by crystallization in toluene three times. HPLC grade chloroform was provided by EM Science. Anhydrous Na₂S was provided by Aldrich. CsF was provided by CABOT, Revene, PA.

Measurements.

GPC analyses were done on an ISCO Model 2300 HPLC pump equipped with two Polymer Laboratories PLgel 5mm MIXED-D 300X7.5 mm columns arranged in series with THF as the eluent and UV detection at 254 nm. The flow rate was set at 1 mL/min. Polystyrene was used as the standard for calibration. DSC thermograms were obtained from Perkin-Elmer Model TGA-7 and Unix DSC 7 or DSC 4 models under nitrogen and air at heating rates of 10 °C/min. NMR experiments were performed at room temperature on a Varian Unity 400 MHz NMR Spectrometers using tetramethylsilane as the internal standard. DSC thermograms were obtained from Perkin-Elmer Model TGA-7 and Unix DSC 7 or DSC 4 models under nitrogen and air at heating rates of 10 °C/min. Rheological experiments were carried out on a Bohlin VOR rheometer with a 25 mm diameter parallel plate fixture. A Bohlin HTC using nitrogen as the heating gas was used for temperature control. About 0.5 g of macrocyclic sample mixed with initiator compressed in a cake was used in the experiments.

The samples were placed between two plates. All the measurements were made under nitrogen atmosphere.

Preparation of Initiators

Fluoride salts and anhydrous sodium sulfide were dissolved in 100 % ethanol to make solutions of 0.02 M and 0.005 M, respectively. Potassium and sodium hydroxide and solutions in 100 % ethanol with a concentration of 0.1 M were accurately titrated with monopotassium isophthalic acid salt. Equivalent amounts of phenol were added to 5.00 mL ethanol solution of the base and the volume was adjusted to 50.00mL with an approximate concentration of 0.01 M initiator.

Ring-opening Polymerization

About 500 mg of macrocycle sample was dissolved in about 5 mL chloroform. Appropriate amounts of initiator solution were added to the chloroform solution and normally the solution remained clear. The solvent was evaporated and dried on a rotatory evaporator at 100 °C for an hour. The sample was transferred to another vial and was dried on the vacuum line at 120 °C overnight until the vacuum was stabilized at ca. 8×10^{-5} torr. The vial was connected to the vacuum line with a vacuum of about 8×10^{-5} torr. It was then loaded onto a preheated aluminum thermal block with the temperature controlled by a thermo-couple. The polymerization was carried out under static vacuum to prevent evaporation of the small sized macrocycle. After the ring-opening polymerization reaction, the sample was dissolved in the about 5 mL THF and

subjected to sonication overnight. Then the soluble part of the sample was subjected to GPC measurements. The high molecular fraction was calculated by integration of the area. The final conversion was calculated by adding the gel fraction which was obtained after repeated washing with THF.

Chapter 7

Synthesis and Characterization of Monodisperse Linear Oligomers of Poly(ether ether ketone)

7.1 Introduction

Poly(ether ether ketone) (PEEK) is a semicrystalline thermoplastic polymer with excellent thermal and mechanical properties.¹ The crystallinity is a key factor contributing to its outstanding properties. This unique polymer has stimulated much study of its crystallization behavior and morphology. The crystal structure of PEEK has been determined by a number of researchers.²⁻⁶ All these studies concluded that the ether and ketone bridges are crystallographically equivalent. Even different poly(arylene ether ketone)s with various placements

[1] May, R. "Encyclopedia of Polymer Science and Engineering", New York, John Wiley & Sons Inc., New York, **1988**, Vol. 12, pp. 313-320.

[2] Dawson, P. C. Blundell, D. J. *Polymer* **1980**, 21, 577.

[3] Rueda, D. R.; Ania F.; Richardson, A.; Ward, I. M.; Balta Caleeja, F. J. *Polym. Commun.* **1983**, 24, 258.

[4] Hay, J. N.; Kemmish, D. J.; Langford, J. I.; Rae, A. I. M. *Polym. Commun.* **1984**, 25, 306.

[5] Wakelyn, N. T. *Polym. Commun.* **1984**, 25, 306.

[6] Fratini, A. V.; Cross, E. M.; Whitaker, R. B.; Adams, W. W. *Polymer* **1986**, 27, 861.

of ketone and ether bridges have space groups similar to that of poly(phenylene oxide). A debatable double endothermic behavior has been observed for samples crystallized from the melt or the glass. A number of suggestions have been proposed to account for this phenomenon, ranging from a melting-recrystallization theory,⁷⁻⁹ to the possible existence of different crystal structures or morphologies.¹⁰⁻¹¹ Most of these studies were based on commercially available PEEK material, which may be subject to variation in molecular weight and its distribution, chain end effects as well as additives. Therefore, it is necessary to have monodisperse PEEK with well-defined end groups in order to exclude the above factors. In addition, the crystal structures of the monodisperse oligomers are expected to be more perfect, which will facilitate the study.

Currently, there has been only one report on the synthesis of monodisperse PEEK oligomers by Jonas and coworkers.¹² An iterative two step

[7] Blundell, D. J.; Osborn, B. N. *Polymer* **1983**, 24, 953.

[8] Blundell, D. J. *Polymer* **1987**, 28, 2248.

[9] Lee, Y.; Porter, R. S. *Macromolecules* **1989**, 22, 1756.

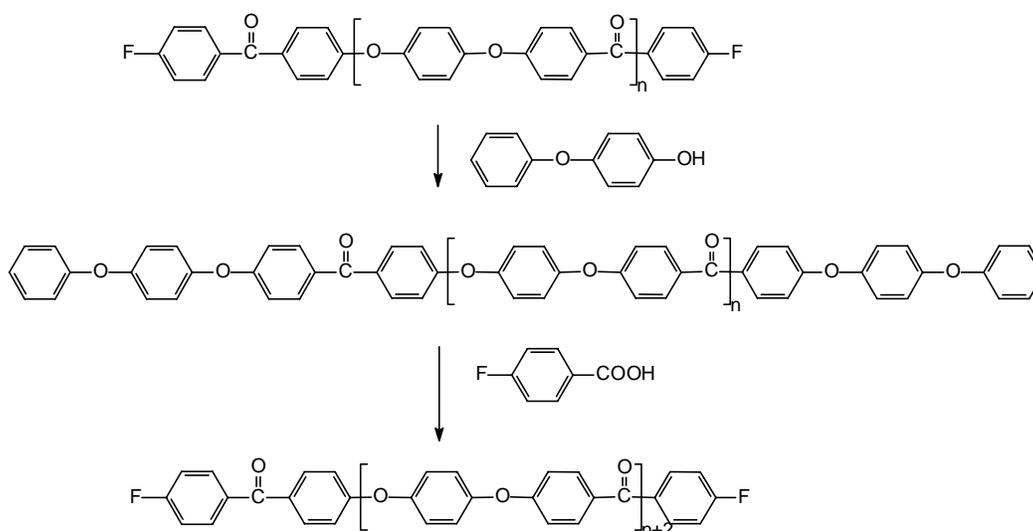
[10] Cheng, S. Z. D.; Cao, M. Y.; Wunderlich, B. *Macromolecules* **1986**, 19, 1868.

[11] Marand, H; Prasad, A. *Macromolecules* **1992**, 25, 1731.

[12] Jonas, A.; Legras, R.; Devaux, J. *Macromolecules* **1992**, 25, 5841.

route was adopted in their work (Scheme 7.1). First, a fluoroaryl ketone terminated n-mer was substituted with 4-phenoxyphenol in the presence of sodium carbonate. The second reaction involved a Friedel-Crafts reaction with 4-fluorobenzoic acid as the acylating agent, trifluoromethanesulfonic acid was used as both the solvent and catalyst.

Scheme 7.1 Iterative Synthesis of PEEK Oligomer

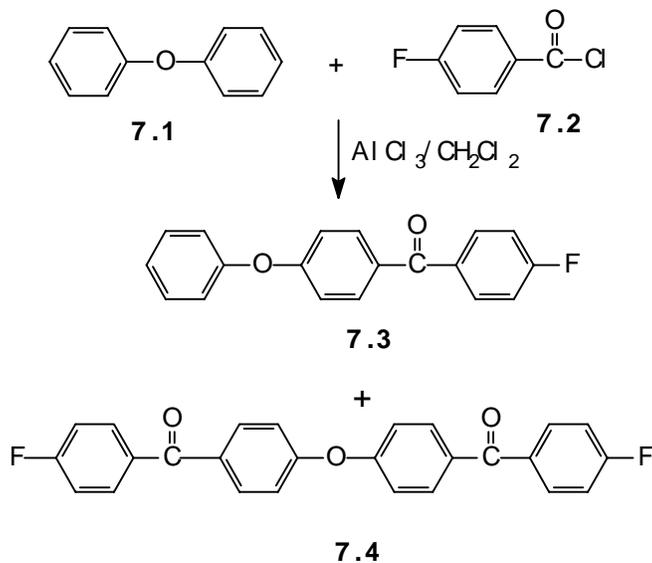


Ideally, starting from 4,4'-difluorobenzophenone and 4,4'-diphenoxybenzene, any number of linear oligomers can be obtained by this method. However, due to the strongly acidic nature of triflic acid, side reactions were observed by both GPC and NMR analyses. The reaction conditions had to be optimized to minimize the side reactions. One obvious fact for the iterative method is that impurities introduced in previous steps will be carried over to the final step. The maximum number of repeating units obtainable was 4. A number of techniques such as NMR, IR and GPC have been used to prove the structures of these linear oligomers. DSC study suggested that there is strong end group

effect on the thermal behaviors of these monodisperse linear oligomers, presumably due to the polar nature of F-C bond. We are interested in synthesizing phenoxy terminated linear oligomers using the nucleophilic aromatic substitution reaction (S_NAr) to compare with the study reported in the literature. The S_NAr reaction involving activated aromatic halide and metallic salts of phenolate is generally a quantitative reaction, which has been widely used to synthesize a number of commercially important high performance polymers including PEEK. Generally this kind of reaction is quite reliable. Our strategy for synthesizing the well-defined PEEK oligomers is a convergent method, which brings together three short pieces to form the final monodisperse linear oligomers.

7.2 Synthesis of Monofluoroaryl Ketone Precursors

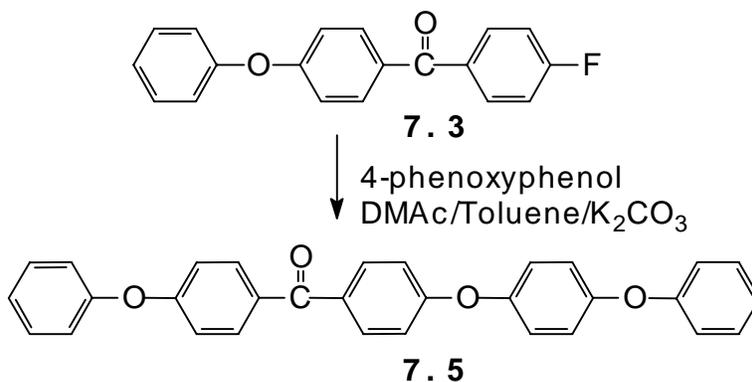
Scheme 7.2



First 4-fluoro-4'-phenoxybenzophenone (**7.3**) was synthesized by Friedel-Crafts acylation (Scheme 7.1). A small amount of **7.4** was filtered out from the hot methanol solution and the last trace of it was removed by column chromatography. The isolated **7.3** had a melting point of 101.8-103.2 °C, which is close to the literature reported value of 101.5-102.0 °C.¹³ Its ^1H NMR spectrum is shown in Figure 7.1. In Figure 7.1, protons H_c , H_d coupled with each other are doublets at $\delta=7.80$ and 7.04 ppm, respectively. H_e is a doublet at $\delta=7.10$ ppm. H_f is a characteristic triplet at 7.41 ppm. H_g is also a triplet at 7.21 ppm. H_a is a triplet at 7.16 ppm due to fluoro-proton coupling. H_b is a doublet of doublets at 7.82 ppm. The coupling pattern is more obvious in the dqcosy spectrum. The ^{13}C NMR spectrum of **7.3** had 17 peaks, which is more than the

number of carbon atoms (13) by four. This can be explained by the additional peaks due to the F-C coupling up to four carbon atoms away. Note that the peak for the carbon attached to H_g is located at 124.61 ppm.

Scheme 7.3



[13] Pews, R. G.; Tsuno, Y.; Taft, R. W. *J. Am. Chem. Soc.*, **1967**, 89, 2391.

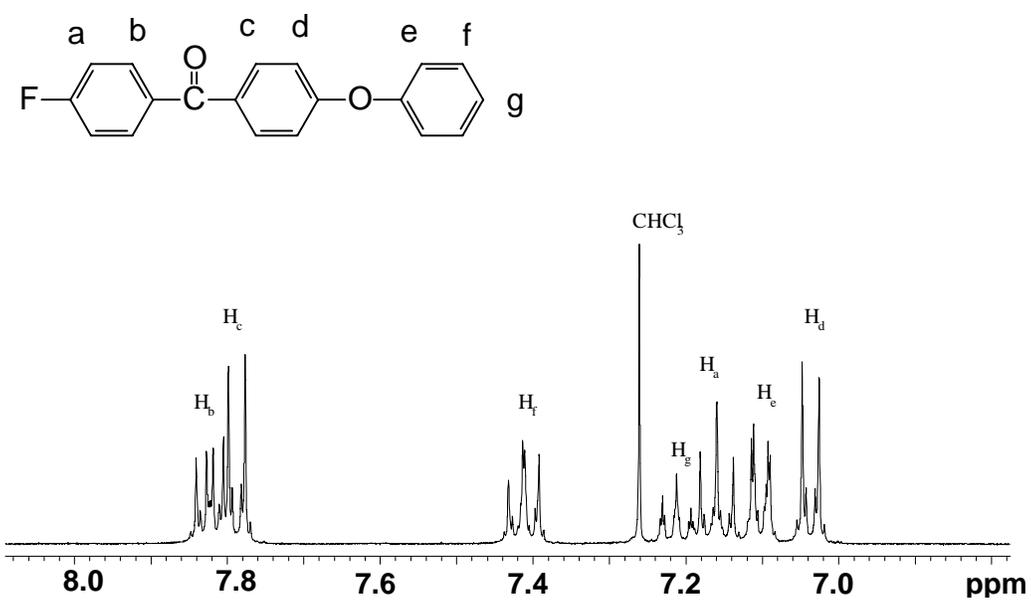


Figure 7.1. 400 MHz ^1H NMR spectrum of 4-fluoro-4'-phenoxybenzophenone in CDCl_3 .

The reaction of 4-phenoxyphenol with **7.3** (Scheme 7.3) was carried out in DMAc by the standard procedures for this type of aromatic nucleophilic substitution reaction. The yield was essentially quantitative. A potential side reaction is the ether exchange reaction. Two side products, i. e., 4,4'-diphenoxybenzophenone and 4,4'-bis(4-phenoxyphenoxy)benzophenone, would be expected if such a side reaction should happen (Scheme 7.3). After the ether exchange reaction, potassium phenoxide would be generated, which could react with the starting material to form 4,4'-diphenoxybenzophenone. The other side product from an ether exchange reaction would react with 4-phenoxyphenol to form 4,4'-bis(4-phenoxyphenoxy)benzophenone. However, no such products were detected by either TLC or NMR. TLC showed just one spot. The ^1H NMR spectrum of the product was clean. This suggests that under the reaction conditions, no ether exchange or any other side reaction has occurred. This is consistent with report that transesterification reaction is only significant at high temperature ($>300\text{ }^\circ\text{C}$). The ^1H NMR spectrum of **7.5** is quite clean (Figure 7.2). Because the benzophenone unit is unsymmetrically substituted, the protons H_g and H_h are two distinct but close doublets located downfield. The signals for the phenoxy unit (H_j , H_k , H_l) are at the same positions as in the starting material **7.3**. New peaks corresponding to the 4-phenoxyphenoxy moiety appear as a triplet at 7.36 ppm (H_b) and another triplet at 7.12 ppm (H_a). H_c is a doublet overlapped with H_j at 7.03 ppm. Because protons H_d and H_e have very close chemical shifts their coupling pattern does not appear as first order. They are located at 7.07

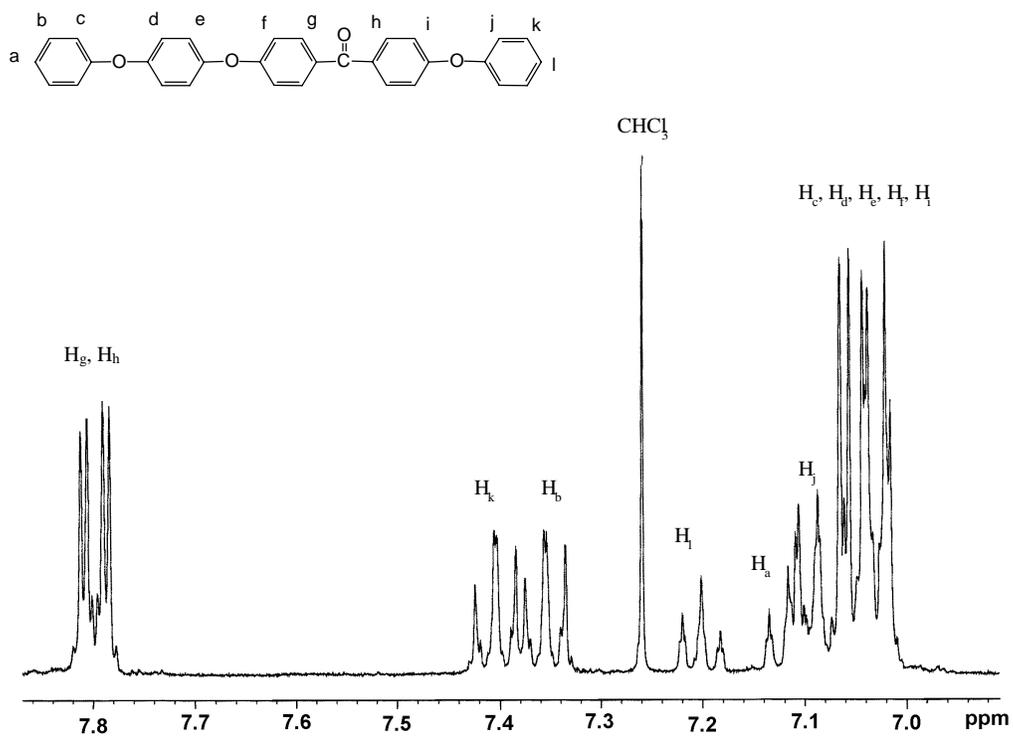
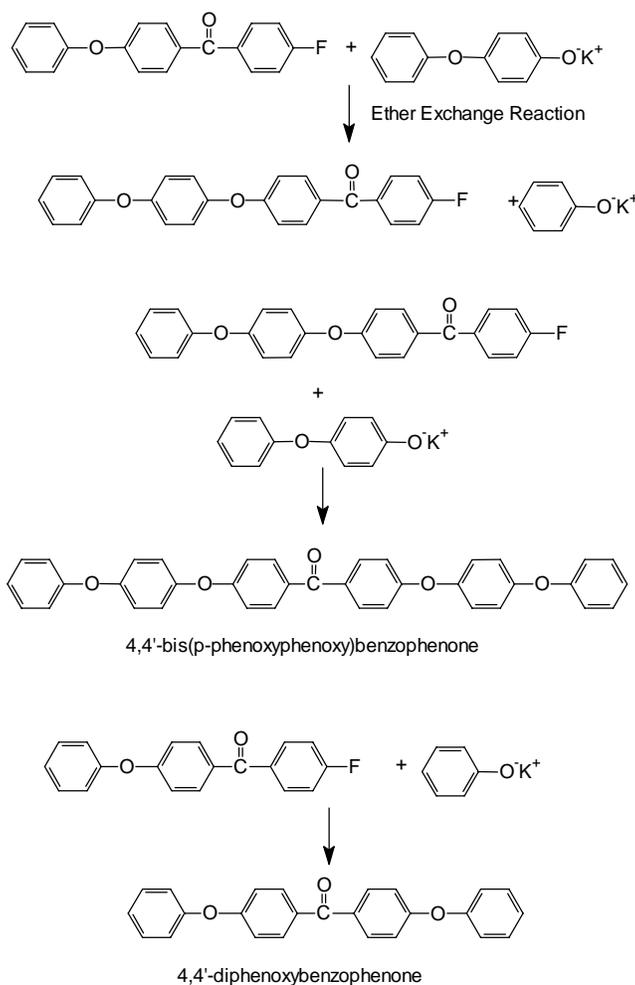


Figure 7.2. 400 MHz ¹H NMR spectrum of compound **7.5** in CDCl₃.

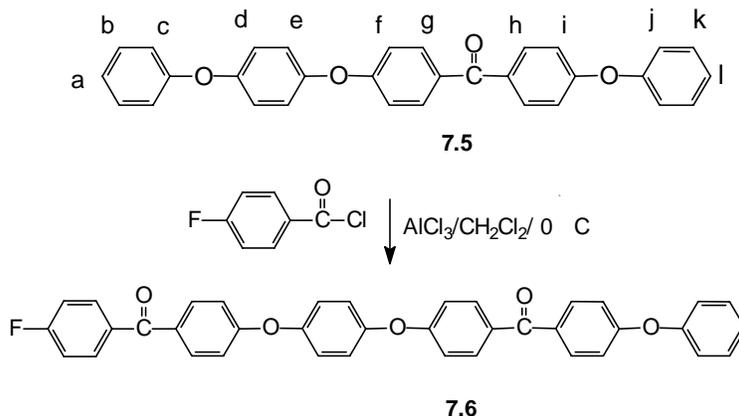
ppm. There are 21 different carbons in the molecule, which matches the number of peaks in the ^{13}C NMR spectrum. In the ^{13}C spectrum the most obvious peak is the carbonyl signal at 194.21 ppm. The signal for C_a is located at 123.29 ppm and C_l is located at 124.61 ppm. These two peaks are used to monitor substitution sites in the subsequent reaction.

Scheme 7.4 Possible Side Products Resulting from Ether Exchange Reactions

Reactions



Scheme 7.5



The key monofluoroaryl ketone precursor **7.6** was synthesized by Friedel-Crafts acylation (Scheme 7.5). It should be pointed out that there are several potential substitution sites. Substitution at positions ortho to the ether linkages is unfavorable due to steric hindrance. This has been proved in our previous syntheses of fluoroaryl ketone monomers. The major question is the competing substitutions at C_a and C_i. The phenoxy group is deactivated by the electron withdrawing carbonyl group, while the phenoxy group in the phenoxyphenoxy moiety is less affected by the carbonyl group. It is expected that the phenoxyphenoxy group is more reactive and thus more susceptible to substitution. In other words, the activation energy is lower. It is a well known physical chemistry principle that lower temperature favors reactions with lower activation energy. Therefore, the reaction was run at 0 °C with the help of an ice water bath. The amount of 4-fluorobenzoyl chloride was slightly less than one equivalent to avoid substitution at the phenoxy unit. The reaction was quenched in concentrated HCl. The crude product was examined with TLC first. TLC indicated that there was a slight excess of starting material left. Recrystallization

in DMAc gave pure product in 67 % yield. The ^1H NMR spectrum (Figure 7.3) of **7.6** shows disappearance of the triplet at $\delta=7.36$ ppm, which is associated with the phenoxyphenoxy moiety in the starting material **7.5**, while the phenoxy group directly attached to the benzophenone unit shows no change in chemical shifts. Therefore, it can be concluded that the substitution exclusively took place at the phenoxyphenoxy moiety. In Figure 7.3, protons H_e and H_f have very similar chemical environments, and they appear only as a characteristic singlet at $\delta=7.14$ ppm. The multiplets near $\delta=7.80$ ppm are due to protons ortho to the electron withdrawing carbonyl groups. The phenoxy moiety has essentially the same chemical shifts as the starting material **7.5**. The ^1H - ^1H dqcosy coupling pattern is fully consistent with the structure. The ^{13}C NMR spectrum (Figure 7.4) has 27 peaks. Again the additional peaks are due to C-F coupling. Note that the peak at $\delta=123.29$ ppm has disappeared while the signal at $\delta=124.61$ ppm is unchanged. This also clearly indicates that the substitution took place exclusively at the phenoxyphenoxy moiety. The product was soluble only in hot DMAc and NMP. The GPC trace of **7.5** shows a sharp single peak (PDI=1.02), which also indicates its high purity. FABMS of this compound gives the quasi-molecular ion peak $[\text{M}+\text{H}]^+$ at $m/z=518.2$ (calculated 518.2).

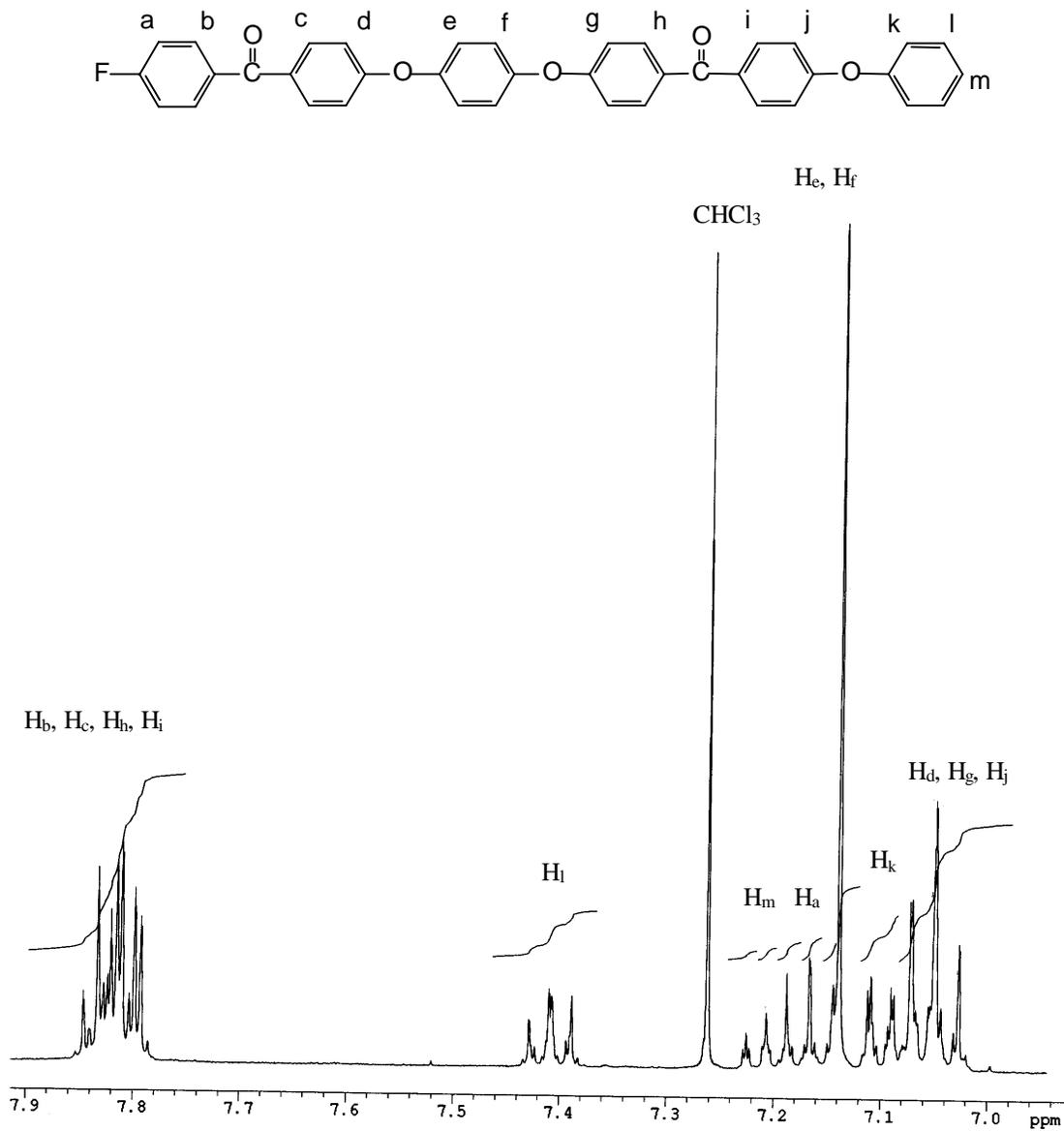


Figure 7.3. 400 MHz ^1H NMR spectrum of monofluoroaryl precursor **7.6** in CDCl_3 .

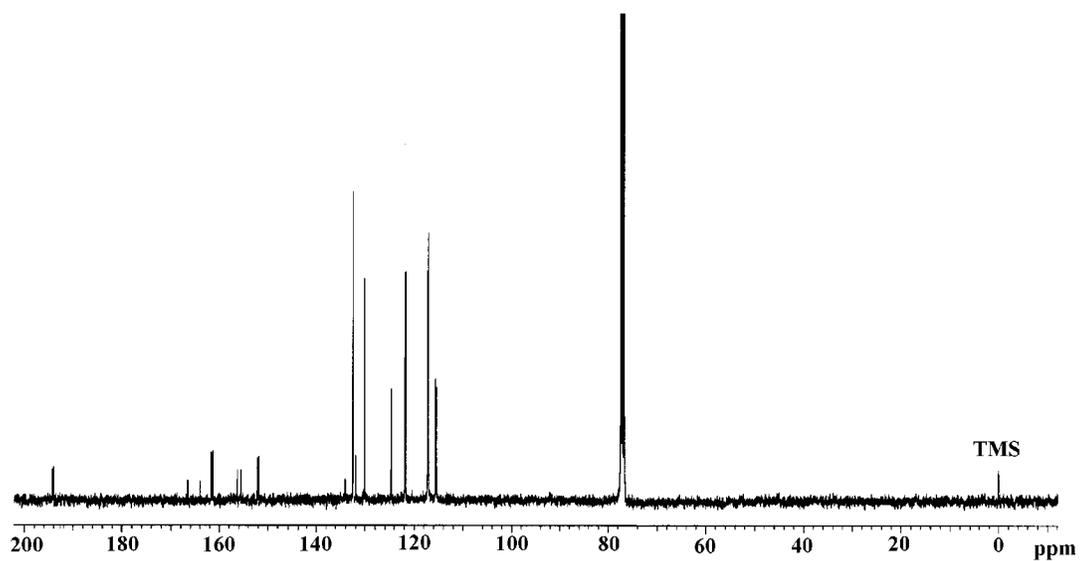
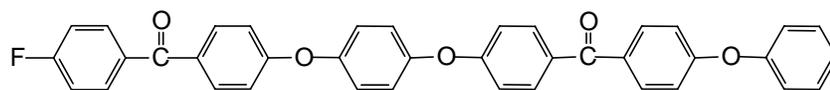
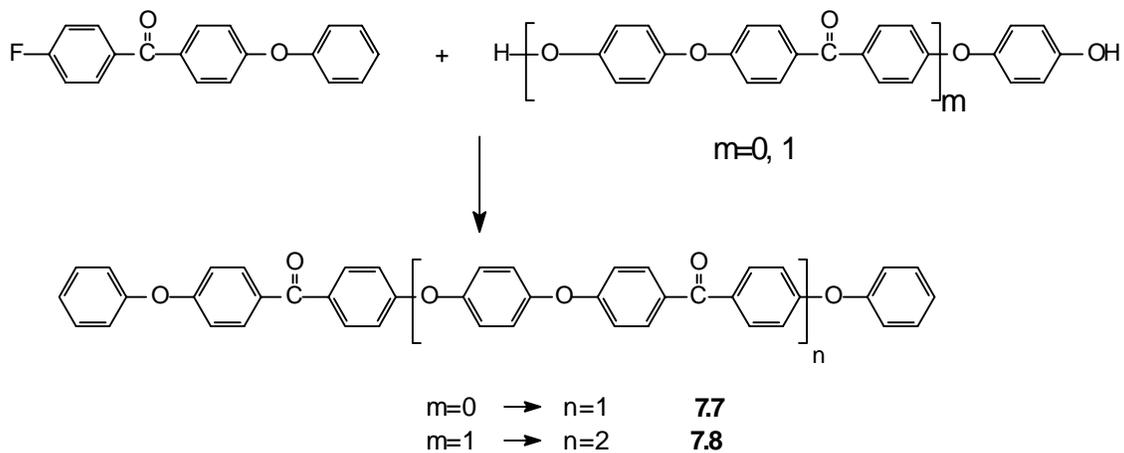


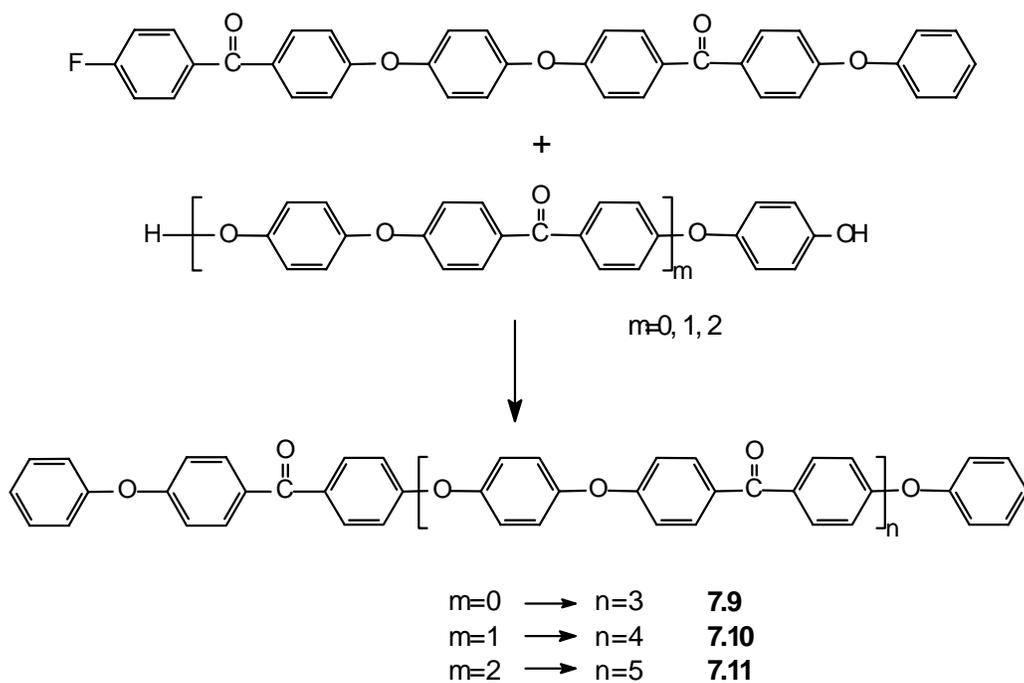
Figure 7.4 100 MHz ^{13}C NMR spectrum of monofluoroaryl precursor **7.6** in CDCl_3 .

7.3 Synthesis of Linear Oligomers with up to 5 Repeating Units

Scheme 7.6



Scheme 7.7



Once the pure monofluoroaryl ketone precursors were obtained, the syntheses of monodisperse oligomers were straightforward. The low molecular weight linear oligomers were obtained by reacting bisphenols with the monofluoroaryl ketone **7.3** or **7.6**. By varying the length of the bisphenol, linear oligomers with up to 5 repeating units can be obtained (Schemes 7.6, 7.7). As discussed previously, the ether exchange reaction is insignificant compared with the normal aromatic substitution reaction involving activated fluoride. Any ether exchange reaction would destroy the monodispersity. It is obvious that in order to get the desired oligomers the reaction should be complete. In most cases ($n=2-5$), the products precipitated out from the solution during the reaction. To examine whether the reaction had indeed been complete, the final product was extracted with hot chloroform. Neither residual starting material **7.3** nor **7.6** (both are soluble in chloroform) was found by TLC. If the reaction were incomplete, the intermediate would be terminated with a phenolic group. However, IR spectra of the final products show no OH group present in the region of 3400 cm^{-1} .

7.3 Characterization of Linear Oligomers

The solubility characteristics (Table 7.1) of the linear oligomers were examined first to find a suitable solvent for the NMR experiments. From Table 7.1, it can be seen that the solubility of the linear oligomers decreases as their length increases. The lower oligomers are soluble in hot dipolar solvents such as DMSO and NMP. Linear oligomers with up to 3 repeating units are soluble in hot NMP. All the linear oligomers have some solubility in methanesulfonic acid.

Table 7.1 Solubility Tests of Linear Oligomers **7.7-7.11**

n	DMSO	NMP	CH ₃ SO ₃ H	CHCl ₃	DMAc
0	yes	yes	yes	yes	yes ^a
1	yes ^a	yes ^a	yes	no	yes ^a
2	yes ^a	yes ^a	yes	no	yes ^b
3	no	yes ^a	yes ^b	no	no
4	no	no	yes ^b	no	no
5	no	no	yes ^b	no	no

a: hot solvent b: slightly soluble n: number of repeating units

These oligomers are highly crystalline compounds; fast atom bombardment mass spectroscopic experiments were not successful to observe the molecular ions of the linear oligomers, presumably due to their insolubility in the matrix as well as the difficulty of overcoming the lattice energy for evaporation.

The ¹³C NMR spectrum of 4,4'-diphenoxybenzophenone was taken first (Figure 7.5). The NMR signals of this compound can be used as reference for the terminal groups in the linear oligomers. The most notable peaks are the carbonyl signal at $\delta=199.71$ ppm and the signal at 169.37 ppm for the ether bridge carbon para to the carbonyl group.

The ¹³C NMR spectrum of linear oligomer **7.7** in methanesulfonic acid is shown in Figure 7.6. There are two peaks around 169 ppm. These peaks are due to the two types of ether bridge carbons, which are para to the carbonyl

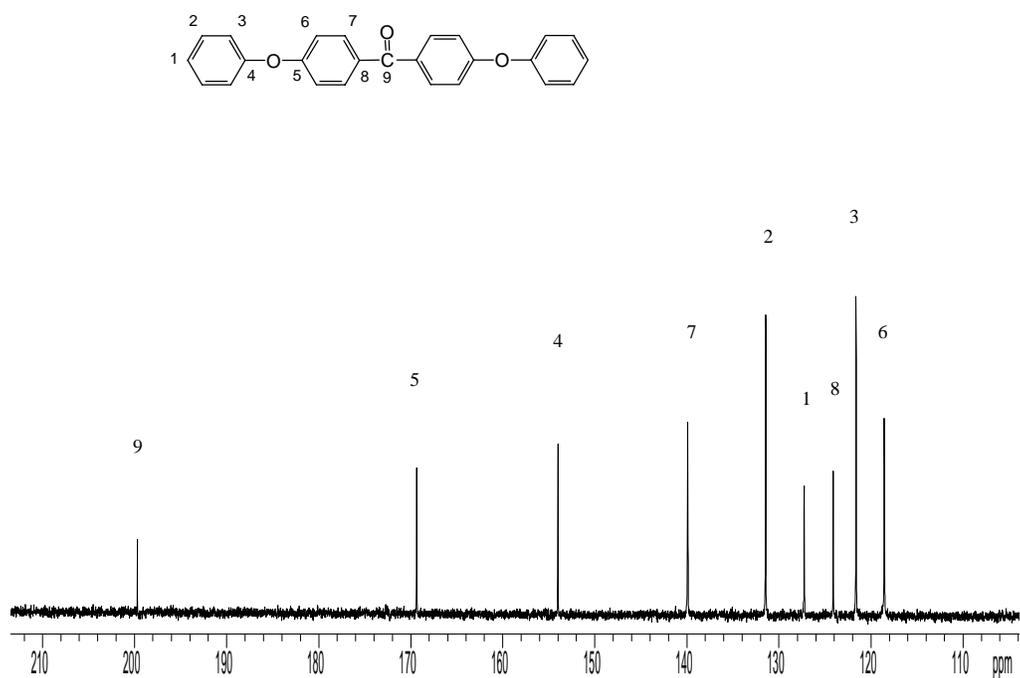


Figure 7.5. 100 MHz ^{13}C NMR spectrum of 4,4'-diphenoxybenzophenone in methanesulfonic acid.

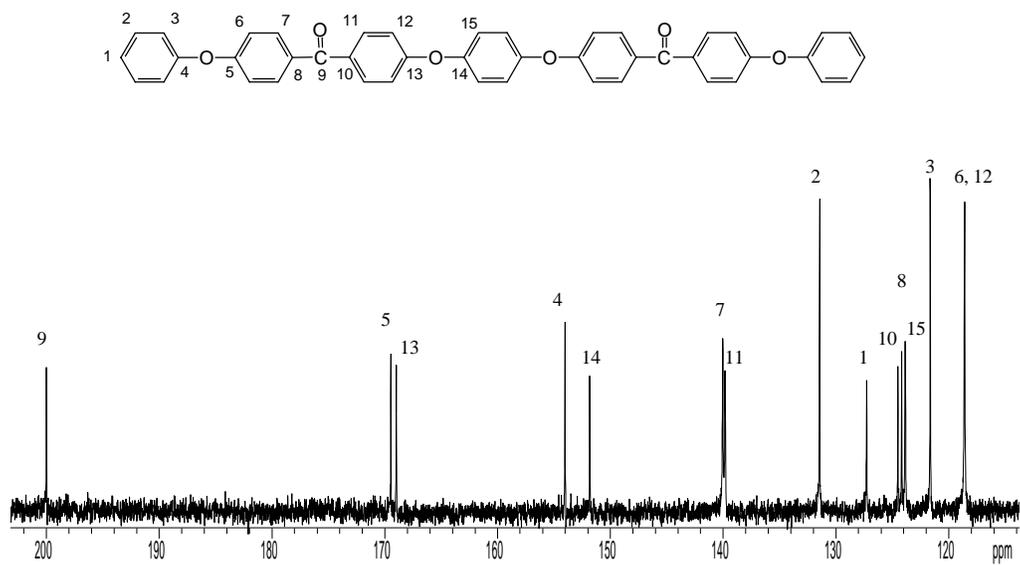


Figure 7.6. 100 MHz ^{13}C NMR spectrum of **7.7** in methanesulfonic acid.

group. All the terminal signals have approximately the same chemical shifts as those of 4,4'-diphenoxybenzophenone. The number of peaks is 14, which is less than the carbon count of 15. This is because two peaks are overlapped at around 118 ppm. The ^{13}C NMR spectrum of **7.8** is shown in Figure 7.7. There are two types of carbonyl groups around 200 ppm. Compared with **7.7**, there is an additional peak around 169 ppm, which is due to the new type of bridge carbon para to the carbonyl group. Again, relative intensities of signals for the terminal groups decrease. All these are consistent with the structure of **7.8**.

The ^{13}C NMR spectra of **7.9-7.11** (Figure 7.8-7.10) are pretty much the same as those of **7.8**. However, the signals for the terminal groups decrease gradually going from **7.9** to **7.11**. The overlapped carbonyl signals at 200.17 ppm increase relative to the terminal carbonyl peak at 199.94 ppm. Most notably, the peak height for the ether bridge carbon at about 169 ppm increases. This is due to the overlapped bridge carbon peaks. In other regions, the peaks are indistinguishable from **7.9** to **7.11**. The low signal/noise ratios of ^{13}C spectra for oligomers **7.10** and **7.11** are due to the low solubilities in methanesulfonic acid.

The elemental analysis results of the high oligomers **7.9-7.11** are close to the calculated values. However, within the experimental errors, these results are not sufficient to distinguish the higher molecular weight oligomers.

All the linear oligomers were further characterized by DSC experiments. The results are summarized in Table 7.2.

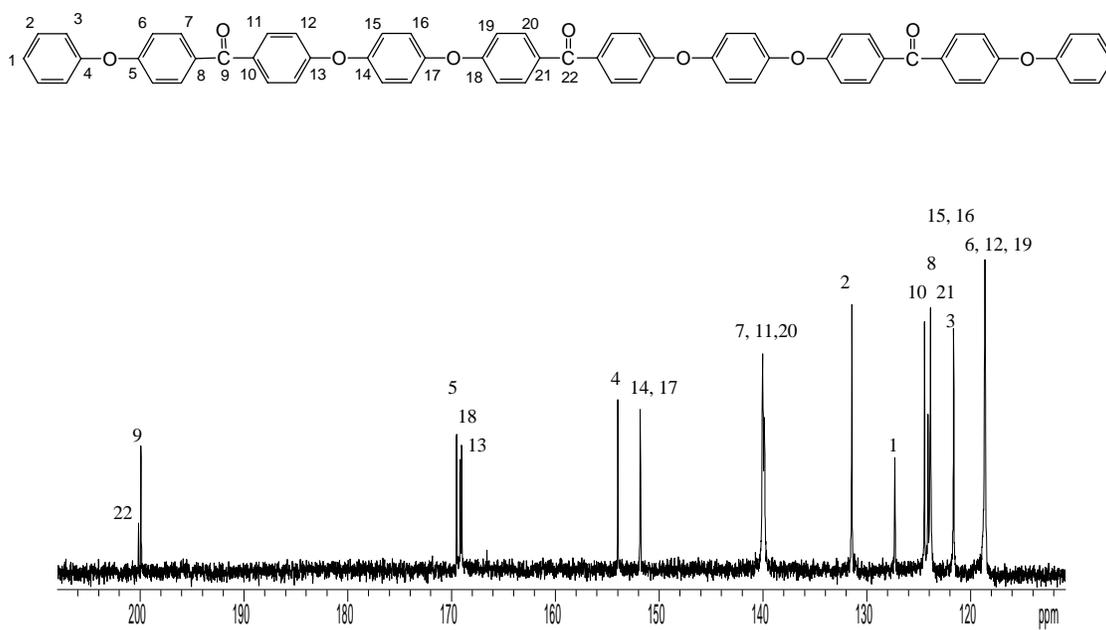


Figure 7.7. 100 MHz ^{13}C NMR spectrum of **7.8** in methanesulfonic acid.

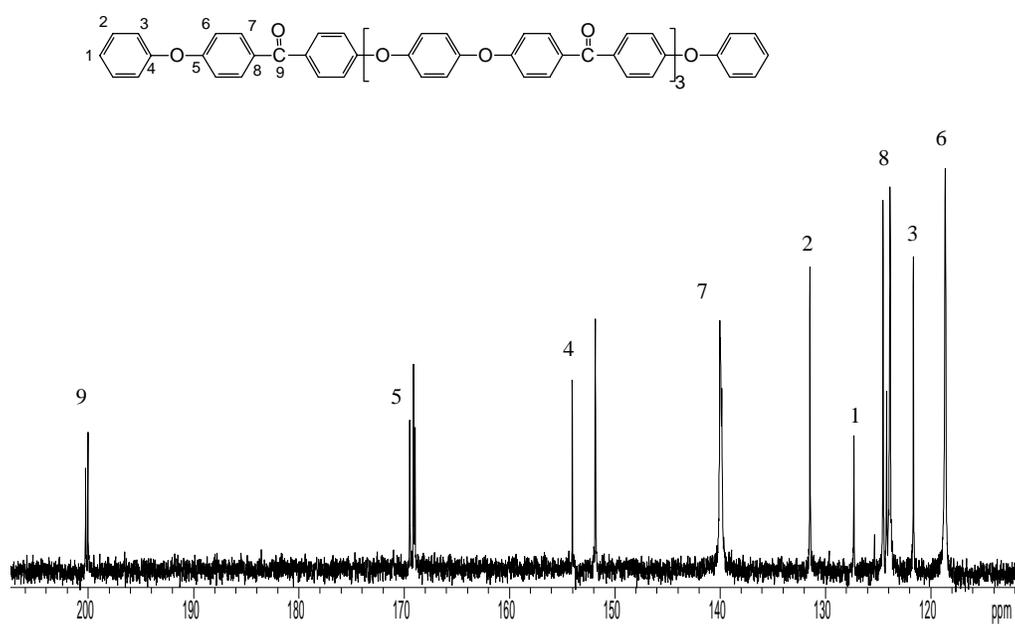


Figure 7.8. 100 MHz ^{13}C NMR spectrum of **7.9** in methanesulfonic acid.

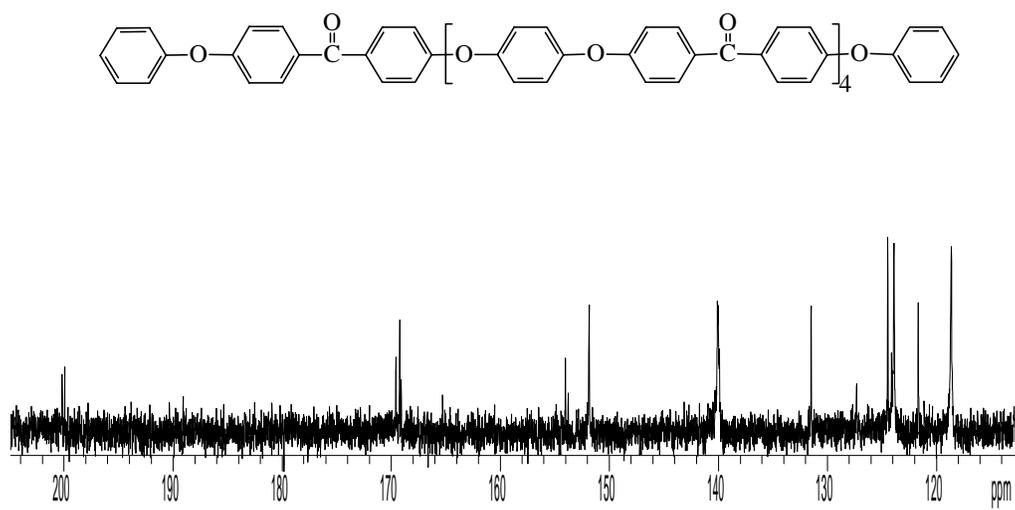


Figure 7.9. 100 MHz ^{13}C NMR spectrum of **7.10** in methanesulfonic acid.

Table 7.2 DSC results of linear oligomers **7.7-7.11**.

n	T _m (°C) ^a	ΔH _m (J/g) ^a	T _c (°C) ^b	ΔH _c (J/g) ^b
1	245.1	142.4	216, 223	-134.1
2	293.3	142.1	252.9	-112.6
3	312.6	138.3	283.7	-107.0
4	322.1	120.0	303.2	-102.1
5	333.5	91.1	305.5	-75.6

a. first heating, rate 10 °C/min b. first cooling, rate 10 °C/min

T_m melting point, T_c crystallization temperature

ΔH_m melting enthalpy, ΔH_c=crystallization enthalpy

The DSC sample of **7.7** was heated up to 300 °C at a rate of 10 °C (Figure 7.11). There is a sharp melting point at 245.1 °C. The melting enthalpy is very high (ΔH_m=142.4 J/g), which is more than what is estimated for 100 % crystallized PEEK (ΔH_m=130 J/mol). There is a small shoulder peak around 240 °C. Upon slowly cooling from the melt, there are two major crystallization peaks at 223 and 216 °C, respectively, and each peak has a shoulder. In the second heating curve, there is only a single melting peak at 241 °C, which is 4 °C lower than the virgin sample. The melting enthalpy is also slightly lower (ΔH_m=136.4 J/g). This indicates that the crystal formed from the melt is less perfect than from solution.

On the first heating curve of DSC thermograms of **7.8** (Figure 7.12), there is only a very sharp melting point at 293.3 °C with a melting enthalpy of

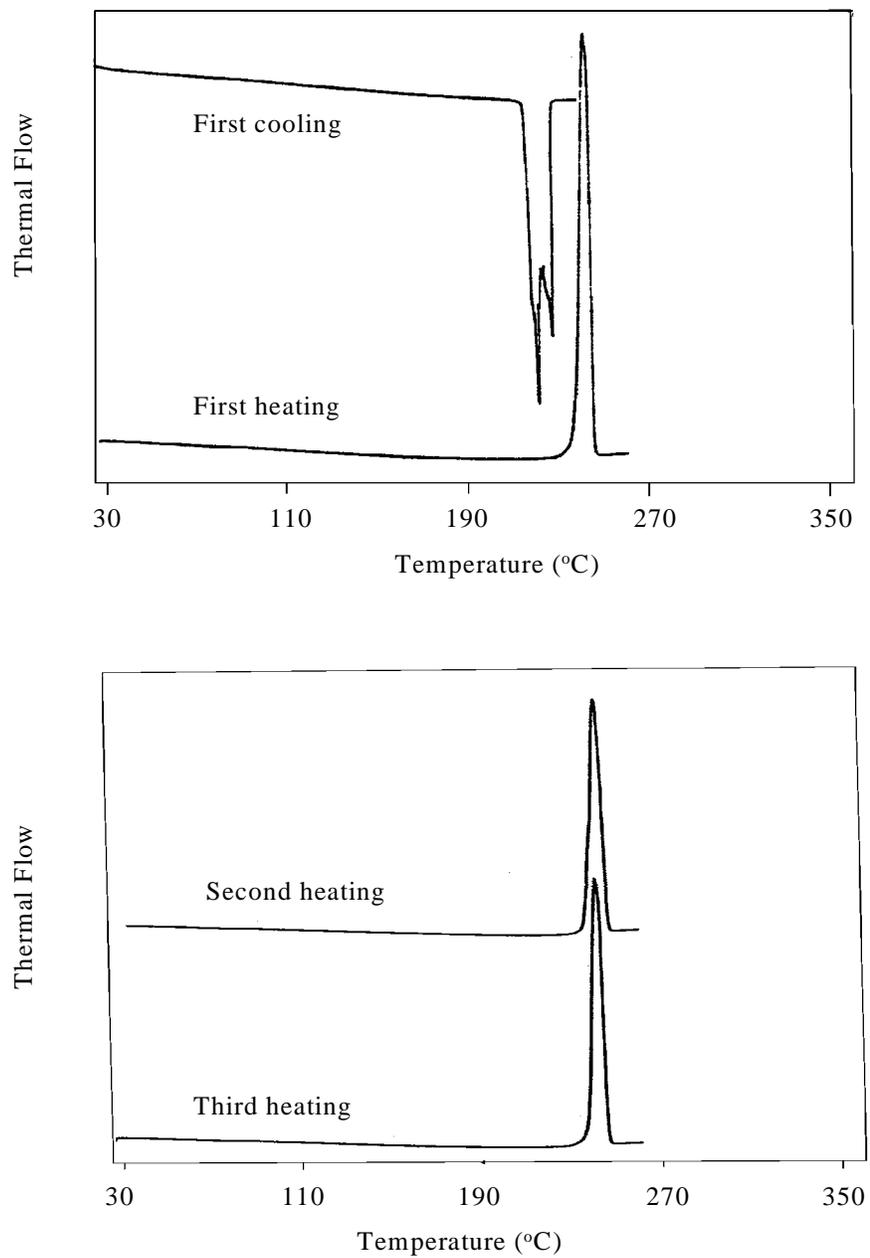


Figure 7.11. DSC thermograms of linear oligomer **7.7**.

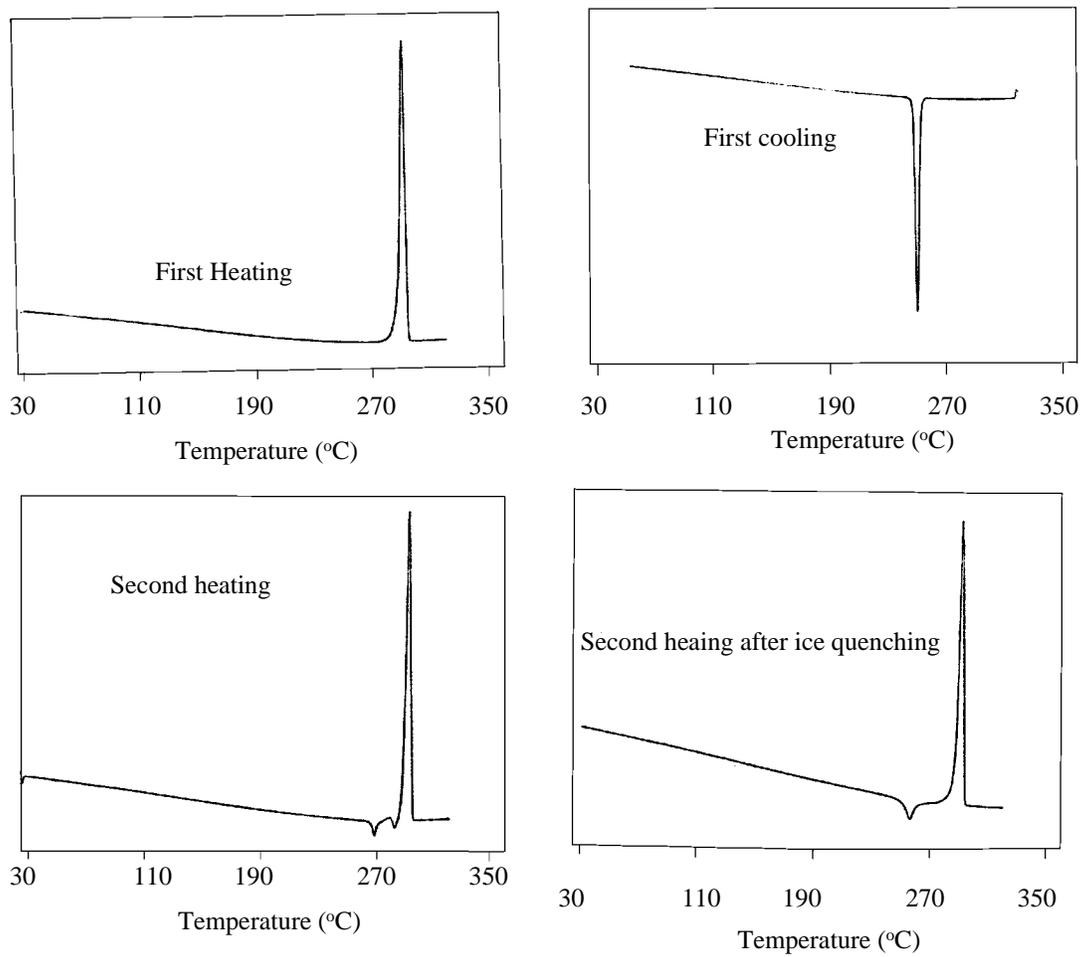


Figure 7.12. DSC thermograms of linear oligomer **7.8**.

142.1 J/g. After staying at 320 °C for about 15 minutes, the sample was cooled to 25 °C at a cooling rate of 10 °C/min. In the cooling curve there is a sharp crystallization peak at 250 °C with a crystallization enthalpy of -112.6 J/g. Upon second heating (10 °C/min), there is a cold crystallization peak at 269 °C ($\Delta H_c = -6.2$ J/g) and a minor melting peak at 279 °C, which is followed by the major melting peak at 293 °C ($\Delta H_m = 129.4$ J/g). The sample was then quenched to room temperature. Upon heating up again, there is a crystallization peak at 256 °C ($\Delta H_c = -14.5$ J/g), which is followed by a single melting peak at 293 °C ($\Delta H_m = 125.7$ J/g). The same sample was held at 320 °C again for 15 minutes followed by slow cooling to 260 °C (10 °C/min). The sample was annealed at this temperature for 60 minutes before being heated again at a rate of 10 °C/min. This time the cold crystallization peak disappeared and the exothermic peak around 279 °C was still there. The major melting peak was almost at the same temperature (293 °C).

The first heating thermogram of virgin sample of **7.9** gives a sharp single melting peak at 312.6 °C with a melting enthalpy of 138.2 J/g (Figure 7.13). Upon cooling, there is a sharp crystallization peak at 284 °C. The melting behavior of the melt crystallized sample is quite different from other samples. On the second heating curve, there are two melting peaks. The low temperature peak is located at 294 °C and the high temperature peak is located at 307 °C. There is an exothermic peak between the two melting peaks, which indicates

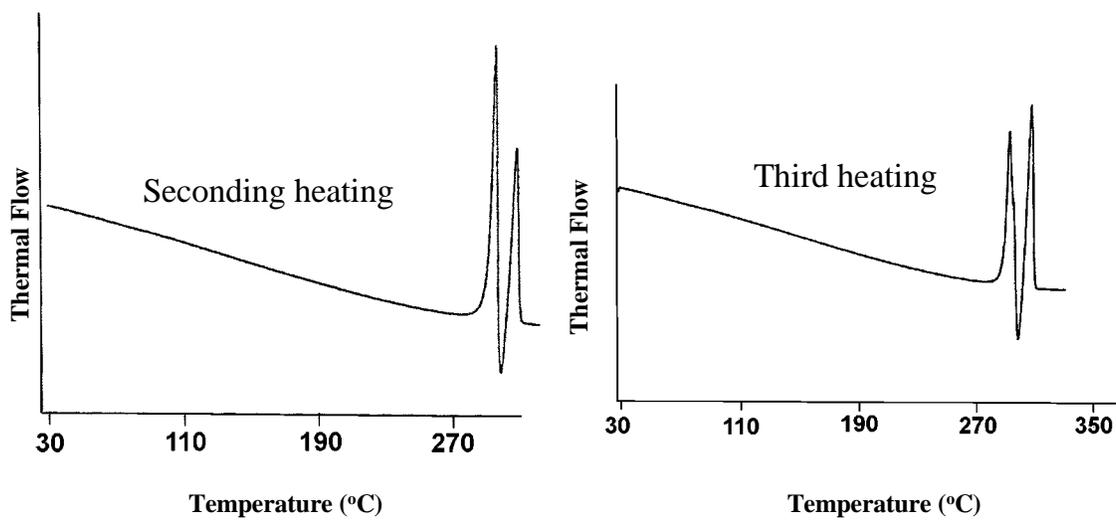
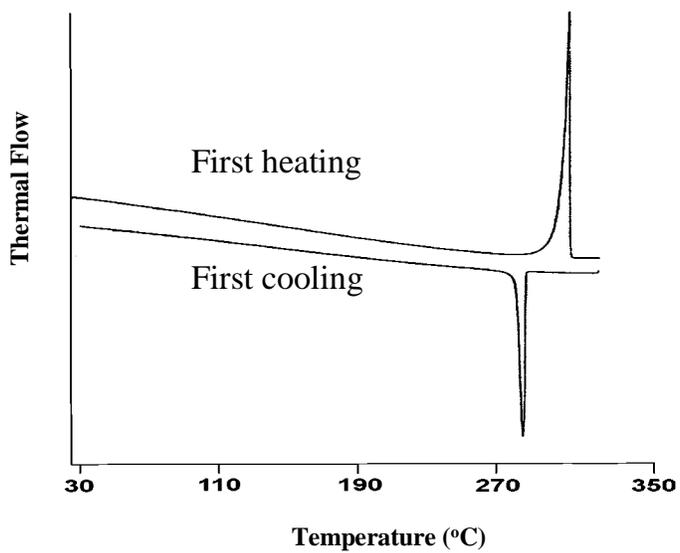


Figure 7.13. DSC thermograms of linear oligomers **7.9**.

some melting-crystallization behavior. These double melting peaks can be seen thereafter independent of the thermal history.

The DSC thermogram of **7.10** shows a sharp melting point at 322 °C with a melting enthalpy of 120 J/g (Figure 7.14). In the cooling curve, there is only a sharp crystallization peak at 303 °C. However, the melt crystallized sample shows a melting peak at 315.1 °C, which is about 7 degrees lower than that of the virgin sample. Thereafter, there is not very much change in melting point and essentially no change in melting enthalpy.

The melting point of **7.11** is broader with a peak value at 333.2 °C. As with the **7.10**, the melting point in the second heating curve after cooling to room temperature at a rate of 10 °C/min is lower by 7 °C.

The change of melting point of a polymer with molecular weight is fit to the following equation.

$$T_m = T_m^0 - A/M$$

Where T_m is the melting point

T_m^0 is the melting point of infinite polymer with infinite molecular weight

M is the molecular weight.

A is a constant related to the terminal groups.

The melting points of the virgin samples are plotted against the reciprocal of molecular weight in Figure 7.15. A good linearity was obtained ($r=0.993$). By curve fitting, the melting point of poly(ether ether ketone) with infinite molecular weight is obtained, which is 383.3 °C.

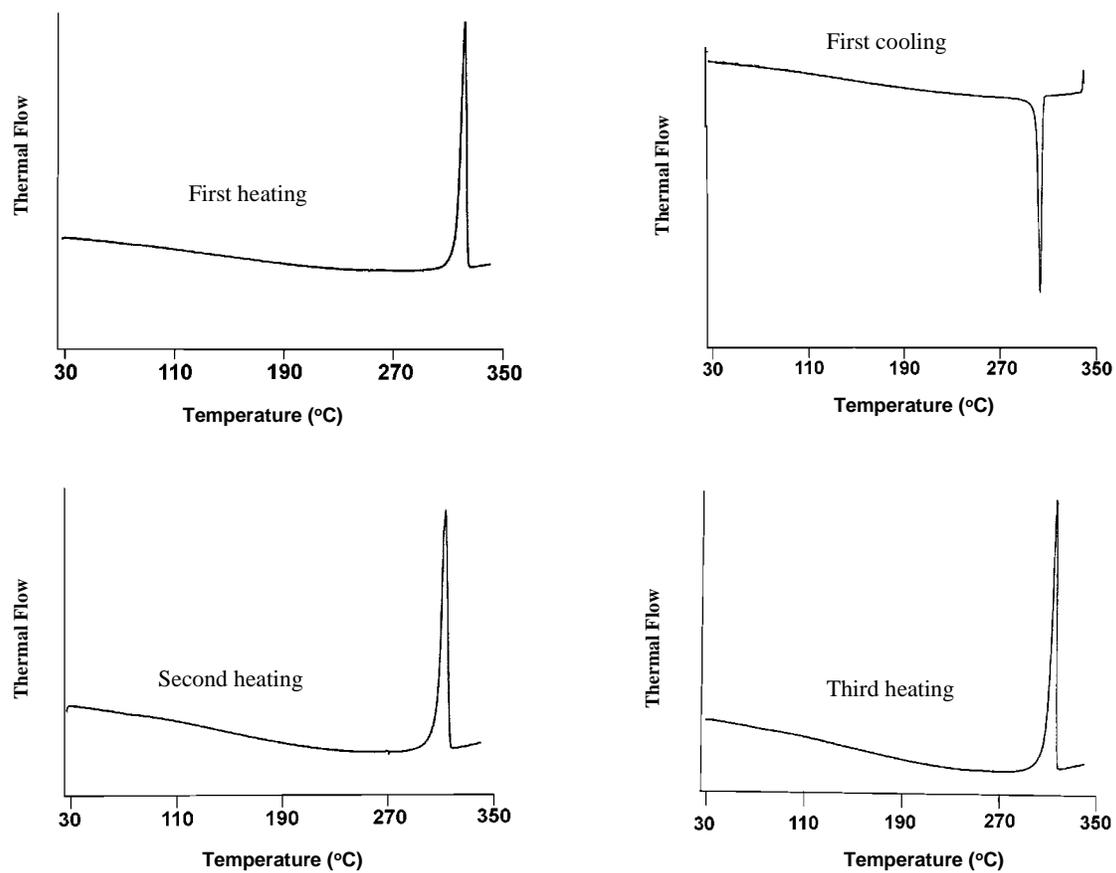


Figure 7.14. DSC thermograms of linear oligomers **7.10**.

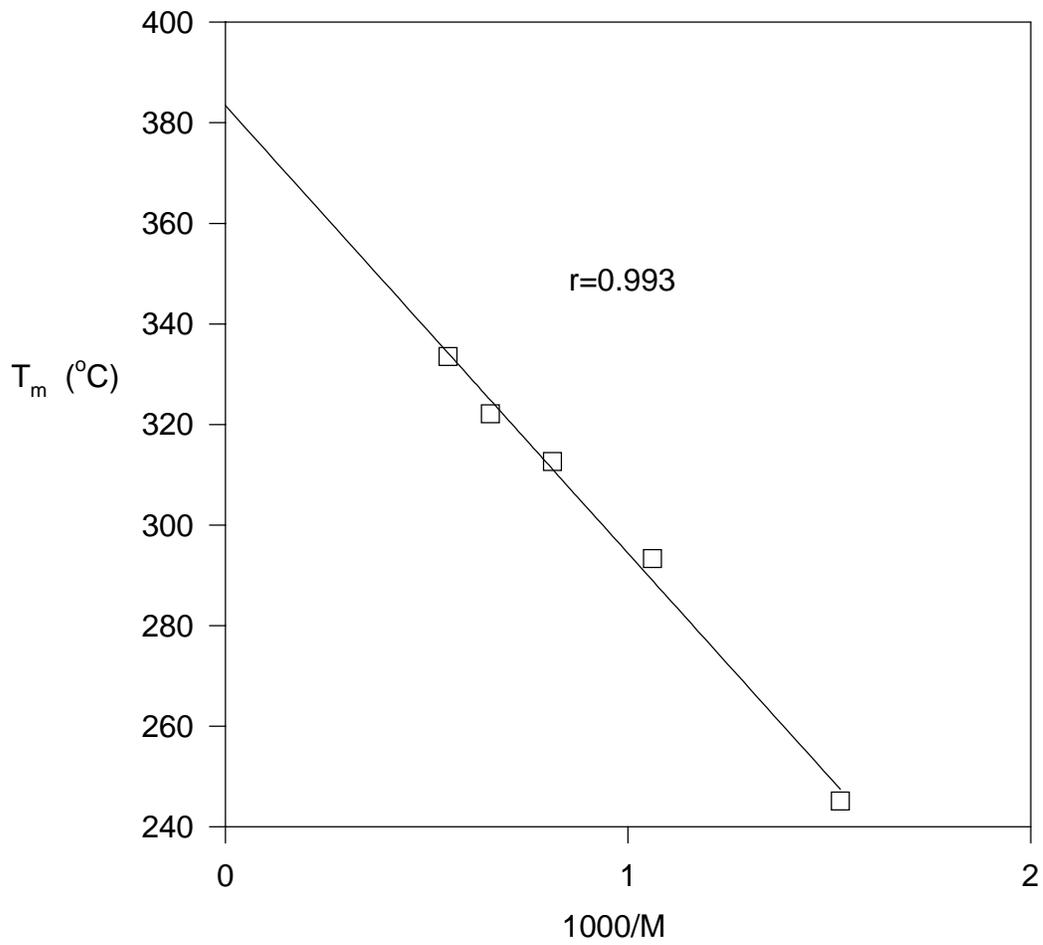


Figure 7.15. Linear plot of melting point vs reciprocal of molecular weight.

7.4 Conclusions

A convergent method has been developed to synthesize monodisperse oligomers with up to five repeating units. The formation of these linear oligomers was confirmed by model studies, elemental and ^{13}C NMR analyses. The monodispersity is ensured by the quantitative nature of the nucleophilic aromatic substitution reaction and the insignificance of the ether exchange reaction at the low reaction temperature. This method can potentially be used to get even longer linear oligomers. The linear oligomers show varied thermal behaviors, which need further detailed study with other methods, such as optical microscopy, X-ray and electron microscopy. Preliminary study suggests that the true thermodynamic melting point of PEEK is around 383 °C and the previously reported melting enthalpy value of 130 J/g is probably underestimated.

7.5 Experimental

Materials: Phenyl ether, hydroquinone and 4-fluorobenzoyl chloride were supplied by Aldrich. DMAc and toluene were provided by Fisher. 4,4'-Bis(4-hydroxyphenoxy)benzophenone and 4,4'-bis((p-(p-hydroxyphenoxy) benzoyl) phenoxy)benzene were synthesized as described in chapter 3. 4-Phenoxyphenol was synthesized by Ullman ether synthesis from phenol and 4-bromophenol.

Measurements: Melting points were determined on a Haake-Buchler capillary melting point apparatus and were corrected unless specified. NMR spectra were taken with a Varian Unity 400 MHz spectrometer. Unless specified, all chemical shifts are relative to TMS in CDCl₃. Elemental analysis results were provided by Atlantic Microlab. DSC was done on a Perkin-Elmer DSC-4 instrument. Infrared spectra (KBr pellets) were recorded on a Nicolet MX-1 FTIR spectrometer.

Synthesis of 4-fluoro-4'-phenoxybenzophenone

To a 250 mL round bottom flask equipped with a magnetic stirrer bar and a condenser were charged 100 mL methylene chloride (dried over P₂O₅), diphenyl ether (10.2g, 60 mmol) and anhydrous AlCl₃ (9.6 g, 72 mmol). The solution was cooled to 0 °C with an ice water bath. 4-Fluorobenzoyl chloride (9.51g, 60 mmol) dissolved in 50 mL methylene chloride was added from a dropping funnel over about 1 hour. The reaction was warmed up to room temperature, kept under stirring overnight and quenched with 20 mL concentrated HCl. Methylene chloride was removed under vacuum. The solid was filtered and washed with excess water. The crude product was washed with 100 mL boiling methanol and insoluble solid was filtered off. Pure product was obtained by column chromatography on silica gel with CH₂Cl₂/hexanes (v/v=4:3).

Yield: 14.1 g (81 %); mp 101.8-103.2 °C (lit. ¹³ mp 101.5-102.0 °C); ¹H NMR (400 MHz, CDCl₃): δ=7.82 (d, J=8.8 Hz, 2H), 7.79 (d, J=8.8 Hz, 2H), 7.41 (d, J=8.8 Hz, 2H), 7.21 (t, J=8.8 Hz, 1H), 7.14 (d, J=8.8 Hz, 2H), 7.11 (d, J=8.8 Hz, 2H), 7.04 (d, J=8.8 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃): δ=194.01, 165.16 (J_{C-F}=253 Hz), 161.66, 155.41, 134.06 (J_{C-F}=3 Hz), 132.35 (J_{C-F}=8 Hz), 132.27, 131.70, 130.03, 124.61, 120.16, 117.14, 115.37 (J_{C-F}=22 Hz).

Synthesis of 4-Phenoxy-4'-(p-phenoxyphenoxy)benzophenone (7.5)

To a 250 mL one neck round bottom flask equipped with a condenser, Dean-Stark trap, N₂ inlet -outlet, and a magnetic stirrer bar were added 4-phenoxyphenol (3.000 g, 16.1 mmol), K₂CO₃ (1.336 g, 9.7 mmol), 100 mL toluene and 50 mL DMAc. The mixture was refluxed for about 4 hours to remove water. After cooling down, 4-fluoro-4'-phenoxybenzophenone (4.709 g, 16.1 mmol) was added. The temperature was kept at reflux again for 18 hours. After toluene was distilled off, the temperature was kept at that of refluxing DMAc for 6 more hours. The product precipitated upon cooling and the total mixture was poured into 1000 mL deionized water, filtered, washed with excess deionized water and dried in a vacuum oven. Yield: 6.79 g (92 %); mp 170.4-173.2 °C (lit.¹⁴, no mp reported); ¹H NMR (400 MHz, CDCl₃): δ=7.80 (two doublets, 4H), 7.40 (t, J=8.8 Hz, 2H), 7.36 (t, J=8.8 Hz, 2H), 7.20 (t, J=8.8 Hz, 1H), 7.12 (t, J=8.8 Hz, 1H), 7.10 (d, J=8.8 Hz, 2H), 7.04 (m, 10H); ¹³C NMR (100 MHz, CDCl₃): δ=194.2 (carbonyl), 161.73, 161.33, 157.30, 155.57, 153.82,

[14] Jonathan R.; Ridd, John H.; Parker, David G.; Rose, John B. *J. Chem. Soc. Perkin Trans.* **1988**, 2, 1735.

150.83, 132.65, 132.21, 132.16, 132.06, 129.99, 129.77, 124.49, 123.29, 121.55, 120.345, 120.06, 118.58, 117.14, 116.66.

Synthesis of Compound 7.6

To a 250 mL round bottom flask equipped with a magnetic stirrer bar, a condenser and N₂ inlet-outlet were added 100 mL methylene chloride (dried over P₂O₅), 4-phenoxy-4'-(p-phenoxyphenoxy)benzophenone (5.46 g, 11.93 mmol) and anhydrous AlCl₃ (3.81 g, 28.6 mmol). The mixture was cooled to 0 °C with an ice water bath. Then 4-fluorobenzoyl chloride (1.89 g, 11.89 mmol) was added. HCl was generated immediately. The solution was stirred at 0 °C for half an hour, room temperature for 2 hours and at reflux for 1 hour. Solvent was evaporated by a rotatory evaporator to get a brown solid, which was quenched with 20 % HCl, filtered and extensively washed with deionized water. The crude product was purified by recrystallization in DMAc. Yield: 4.65 g (67 %); mp 220.4-222.9 °C; ¹H NMR: δ=7.82 (m, 8H), 7.41 (t, J=8.8 Hz, 2H), 7.21 (t, J=8.8 Hz, 1H), 7.17 (t, J=8.8 Hz, 2H), 7.14 (s, 4H), 7.10 (d, J=8.8 Hz, 2H), 7.05 (m, 6H); ¹³C NMR (400 Hz, CDCl₃): δ=194.22 (carbonyl), 193.98 (carbonyl), 166.50, 163.97, 161.70, 161.46, 161.34, 155.58, 152.19, 151.91, 134.06, 132.45, 132.37, 132.29, 132.23, 132.14, 131.92, 130.06, 124.57, 121.76, 121.67, 120.14, 117.19, 117.03, 117.00, 115.56, 115.34.

Synthesis of Linear Oligomer 7.7

To a 100 mL round bottom flask equipped with a Dean-Stark trap, a condenser, N₂ inlet-outlet and a magnetic stirrer were added 40 mL DMAc and 20 mL toluene. The solution was azeotropically refluxed for 4 hours before 4-fluoro-4'-phenoxybenzophenone (1.46 g, 5 mmol), hydroquinone (0.2753 g, 2.5

mmol) and K_2CO_3 (1.4146 g, 3 mmol) were added. The reaction was kept at reflux for 16 hours before toluene was distilled off and continued for 8 more hours. The DMAc solution was poured into deionized water. The solid product was filtered and washed with excess water. The final product was obtained by recrystallization in DMAc. Yield 1.40 g (86 %); mp 244.1-245.2 °C (uncorrected); ^{13}C NMR (100 MHz, CH_3SO_3H): δ =200.02, 169.48, 168.99, 154.03, 151.83, 140.04, 139.84, 131.47, 127.29, 124.52, 124.18, 123.86, 121.65, 118.61.

Synthesis of Linear Oligomer 7.8

The synthetic procedures were similar to those for **7.7**. After completion of the reaction, the product precipitated out from DMAc solution, which was filtered, washed with excess water and recrystallized in NMP. Yield: 2.15 g (91 %); mp 291.1-291.8 °C (uncorrected); ^{13}C NMR (100 MHz, CH_3SO_3H): δ =200.17, 199.94, 169.52, 169.19, 169.05, 154.00, 151.82, 140.06, 139.88, 131.46, 127.30, 124.46, 124.12, 123.88, 121.65, 118.61.

Synthesis of Linear Oligomer 7.10

To a 500 mL round bottom flask equipped with a Dean-Stark trap, a condenser, N_2 inlet-outlet, and a magnetic stirrer bar, were added 4,4'-bis(p-hydroxyphenoxy)benzophenone (0.3431g, 0.86 mmol), K_2CO_3 (0.1430 g, 1.03 mmol), 200 mL DMAc and 100 mL toluene. The mixture was azeotropically distilled for two hours to remove water. After cooling down, **7.6** (1.000 g, 1.72 mmol) was added. The solution was clear at first. Some product precipitated

out during the reaction. After about 9 hours, toluene was distilled off. The reaction was kept at reflux for 30 hours. DMAc was removed by a rotatory evaporator to get a solid, which was washed extensively with water. The dried sample was further washed with refluxing methanol, acetone, DMAc and NMP. Yield: 1.24 g (95 %); mp 320.0-323.0 °C (uncorrected).

Elemental Analysis for $C_{101}H_{66}O_{15}$ Calc: C 79.83 H 4.38 O 15.59

Found: C 79.66 H 4.62

Synthesis of Linear Oligomer 7.9

The synthetic procedures were similar to those for **7.10**. The oligomer **7.9** was purified by recrystallization in NMP, mp 311.3-314.5 °C (uncorrected); IR (KBr pellet) 1642, 1599, 1231, 1161, 929, 842, 767, 517.

Elemental Analysis for $C_{82}H_{54}O_{12}$ Calc: C 79.99 H 4.42 O 15.59

Found: C 80.09 H 4.40

Synthesis of Linear Oligomer 7.11

The synthetic procedures were similar to those for **7.10**. NMP was used as the solvent, in which the linear oligomers are more soluble, to ensure that the reaction was complete. The final product was recrystallized in phenol/1,3,5-trichlorobenzene (v/v=1:1) and the crystals were washed with acetone. IR (KBr pellet): 1642, 1599, 1490, 1231, 1161, 929, 842, 767, 518.

Elemental Analysis for $C_{120}H_{78}O_{18}$ Calc: C 79.72 H 4.35 O 15.93

Found: C 79.60 H 4.46

Chapter 8 Future Work

Based upon this work, the following directions of research in the macrocyclic technique are suggested.

The excellent yields of cyclic poly(ether ketone) or sulfones are quite unusual. Our preliminary computer modeling study suggests that there is some kind of templating effect. If a carbonate ion is placed in the middle of a macrocycle the total energy is reduced. This phenomenon needs further study.

We have shown that the size distribution can be controlled by the linear oligomeric precursor approach. This has effectively reduced the amount of double sized macrocycle. However, this technique is not applicable to some systems such as poly(ether ether ketone)s because the linear oligomers can not be obtained quantitatively due to the solubility problem. To avoid this problem use of the difluoroketimine is suggested.

Although, it is possible to get reasonably high molecular weight polymer using appropriate amounts of initiators at appropriate temperatures, the crosslinking of the final polymer is a general phenomenon. There is a need for the detailed ring-opening mechanism study to elucidate the crosslinking mechanism and thus to find a possible solution to a controllable polymerization and possible pseudo-living polymerization.

From an economics point of view, due to the pseudo-high dilution reaction conditions, the cost of making these kinds of cyclic monomers is quite high. In the foreseeable future, it is unrealistic to see commercial application of this

technique. However, using a small amount of these cyclics to blend with some other polymers and then polymerize the macrocycles to form composite materials is possible. MacKnight's group at University of Massachusetts has shown the promise of this technique.¹

We have yet to demonstrate the superior or equivalent performance of these materials as adhesives or matrix materials. In order to do this, serious collaboration from other groups with expertise in polymer processing is needed.

The extension of this macrocyclic monomer for polyester liquid crystal systems is another direction we should look at. As mentioned earlier, the ring-opening polymerization of this type of precursor to form a separate liquid crystalline phase can probably be used to form molecular composites.

[1] Nachlis, W. L.; Kambour, R. P.; MacKnight, W. J. *Polymer* **1994**, 17, 3643.

Appendix A: X-ray Structure Data of Macrocycle 2.9 (n=1)Coordinates ($\times 10^{-4}$) and Equivalent Isotropic Thermal Parameters ($\times 10^{-3}$)

Atom	x	y	z	U (eq)
O (1)	5655 (3)	5558 (2)	-1233 (5)	47 (2)
O (2)	1830 (3)	5394 (2)	149 (5)	44 (2)
O (3)	-1317 (4)	7621 (2)	-4074 (5)	49 (2)
C (1)	5107 (4)	5836 (2)	-1505 (7)	30 (2)
C (2)	2708 (5)	5767 (2)	-1412 (7)	36 (2)
C (3)	3520 (5)	5879 (2)	-1791 (8)	36 (2)
C (4)	4223 (4)	5755 (2)	-1107 (8)	33 (2)
C (5)	4098 (4)	5514 (2)	-14 (8)	39 (2)
C (6)	3299 (5)	5402 (2)	411 (7)	35 (2)
C (7)	2602 (4)	5528 (2)	-315 (8)	34 (2)
C (8)	-54 (5)	6021 (2)	-786 (8)	42 (2)
C (9)	701 (5)	5920 (2)	-251 (8)	44 (2)
C (10)	1085 (4)	5514 (3)	-482 (7)	32 (2)
C (11)	703 (5)	5198 (3)	-1275 (8)	46 (2)
C (12)	-62 (5)	5303 (2)	-1814 (7)	36 (2)
C (13)	-477 (4)	5712 (2)	-1565 (7)	31 (2)
C (14)	-1367 (4)	5818 (2)	-2051 (8)	35 (2)
C (15)	-1966 (5)	5764 (2)	-927 (7)	38 (2)
C (16)	-1655 (5)	5471 (2)	-3013 (7)	36 (2)
C (17)	-1533 (5)	7124 (2)	-2321 (8)	36 (2)
C (18)	-1557 (5)	6677 (2)	-1855 (8)	36 (2)
C (19)	-1385 (4)	6306 (2)	-2585 (8)	29 (2)
C (20)	-1197 (5)	6385 (2)	-3816 (8)	37 (2)
C (21)	-1169 (5)	6823 (3)	-4280 (8)	41 (2)
C (22)	-1325 (5)	7190 (2)	-3555 (8)	36 (2)
C (23)	98 (5)	8347 (2)	-2244 (7)	38 (2)
C (24)	-209 (5)	7961 (2)	-2821 (8)	46 (2)
C (25)	-984 (5)	7979 (2)	-3381 (8)	38 (2)
C (26)	-1463 (5)	8380 (2)	-3386 (7)	37 (2)
C (27)	-1152 (4)	8754 (2)	-2802 (7)	33 (2)
C (28)	-360 (4)	8751 (2)	-2205 (7)	32 (2)
C (30)	1586 (4)	6744 (2)	-4126 (6)	376 (27)
Cl (1)	990 (4)	6666 (3)	-2724 (8)	308 (5)
Cl (2)	2694 (3)	6786 (2)	-3762 (9)	305 (5)
Cl (3)	1245 (4)	7257 (2)	-4883 (5)	244 (3)

Bond length (Å)

Bond	Length
O(1)-C(1)	1.227(8)
O(2)-C(7)	1.376(8)
O(2)-C(10)	1.407(8)
O(3)-C(22)	1.387(8)
O(3)-C(25)	1.396(9)
C(1)-C(28) #1	1.487(10)
C(1)-C(4)	1.482(10)
C(2)-C(3)	1.387(10)
C(2)-C(7)	1.391(10)
C(3)-C(4)	1.383(10)
C(4)-C(5)	1.393(10)
C(5)-C(6)	1.384(10)
C(6)-C(7)	1.403(10)
C(8)-C(9)	1.359(10)
C(8)-C(13)	1.409(10)
C(9)-C(10)	1.364(9)
C(10)-C(11)	1.401(10)
C(11)-C(12)	1.377(10)
C(12)-C(13)	1.395(9)
C(13)-C(14)	1.535(10)
C(14)-C(16)	1.529(10)
C(14)-C(19)	1.548(9)
C(14)-C(15)	1.550(10)
C(17)-C(22)	1.388(10)
C(17)-C(18)	1.410(10)
C(18)-C(19)	1.375(10)
C(19)-C(20)	1.383(10)
C(20)-C(21)	1.383(10)
C(21)-C(22)	1.359(10)
C(23)-C(24)	1.385(10)
C(23)-C(28)	1.392(9)
C(24)-C(25)	1.367(11)
C(25)-C(26)	1.402(10)
C(26)-C(27)	1.361(10)
C(27)-C(28)	1.410(10)
C(28)-C(1) #1	1.487(10)
C(30)-Cl(1)	1.7999(10)
C(30)-Cl(2)	1.8001(10)
C(30)-Cl(3)	1.8000(10)

Bond Angles (°)

C(7)-O(2)-C(10)	119.6(6)
C(22)-O(3)-C(25)	118.4(6)
O(1)-C(1)-C(28)#1	118.5(6)
O(1)-C(1)-C(4)	119.3(7)
C(28)#1-C(1)-C(4)	122.2(6)
C(3)-C(2)-C(7)	119.0(7)
C(2)-C(3)-C(4)	121.4(7)
C(3)-C(4)-C(5)	118.4(7)
C(3)-C(4)-C(1)	124.0(7)
C(5)-C(4)-C(1)	117.5(7)
C(6)-C(5)-C(4)	122.2(7)
C(5)-C(6)-C(7)	117.9(7)
O(2)-C(7)-C(2)	124.3(7)
O(2)-C(7)-C(6)	114.6(7)
C(2)-C(7)-C(6)	121.1(7)
C(9)-C(8)-C(13)	122.0(7)
C(10)-C(9)-C(8)	120.2(7)
C(9)-C(10)-O(2)	120.2(7)
C(9)-C(10)-C(11)	120.1(7)
O(2)-C(10)-C(11)	119.5(6)
C(12)-C(11)-C(10)	119.2(7)
C(11)-C(12)-C(13)	121.6(7)
C(12)-C(13)-C(8)	116.7(7)
C(12)-C(13)-C(14)	122.7(7)
C(8)-C(13)-C(14)	120.5(6)
C(16)-C(14)-C(13)	111.7(6)
C(16)-C(14)-C(19)	111.2(6)
C(13)-C(14)-C(19)	109.5(6)
C(16)-C(14)-C(15)	106.5(6)
C(13)-C(14)-C(15)	105.6(6)
C(19)-C(14)-C(15)	112.2(6)
C(22)-C(17)-C(18)	118.7(7)
C(19)-C(18)-C(17)	122.0(8)
C(20)-C(19)-C(18)	117.5(7)
C(20)-C(19)-C(14)	120.8(6)
C(18)-C(19)-C(14)	121.7(8)
C(21)-C(20)-C(19)	120.8(7)
C(22)-C(21)-C(20)	121.7(8)
C(21)-C(22)-O(3)	119.5(8)
C(21)-C(22)-C(17)	119.1(7)
O(3)-C(22)-C(17)	121.3(7)
C(24)-C(23)-C(28)	122.1(7)
C(25)-C(24)-C(23)	118.9(7)
C(24)-C(25)-C(26)	121.2(7)
C(24)-C(25)-O(3)	123.1(7)
C(26)-C(25)-O(3)	115.4(7)
C(27)-C(26)-C(25)	118.9(7)
C(26)-C(27)-C(28)	121.9(7)
C(23)-C(28)-C(27)	117.0(7)
C(23)-C(28)-C(1)#1	125.0(7)
C(27)-C(28)-C(1)#1	117.9(6)

C(7)-O(2)-C(10)	119.6(6)
C(22)-O(3)-C(25)	118.4(6)
O(1)-C(1)-C(28)#1	118.5(6)
O(1)-C(1)-C(4)	119.3(7)
C(28)#1-C(1)-C(4)	122.2(6)
C(3)-C(2)-C(7)	119.0(7)
C(2)-C(3)-C(4)	121.4(7)
C(3)-C(4)-C(5)	118.4(7)
C(3)-C(4)-C(1)	124.0(7)
C(5)-C(4)-C(1)	117.5(7)
C(6)-C(5)-C(4)	122.2(7)
C(5)-C(6)-C(7)	117.9(7)
O(2)-C(7)-C(2)	124.3(7)
O(2)-C(7)-C(6)	114.6(7)
C(2)-C(7)-C(6)	121.1(7)
C(9)-C(8)-C(13)	122.0(7)
C(10)-C(9)-C(8)	120.2(7)
C(9)-C(10)-O(2)	120.2(7)
C(9)-C(10)-C(11)	120.1(7)
O(2)-C(10)-C(11)	119.5(6)
C(12)-C(11)-C(10)	119.2(7)
C(11)-C(12)-C(13)	121.6(7)
C(12)-C(13)-C(8)	116.7(7)
C(12)-C(13)-C(14)	122.7(7)
C(8)-C(13)-C(14)	120.5(6)
C(16)-C(14)-C(13)	111.7(6)
C(16)-C(14)-C(19)	111.2(6)
C(13)-C(14)-C(19)	109.5(6)
C(16)-C(14)-C(15)	106.5(6)
C(13)-C(14)-C(15)	105.6(6)
C(19)-C(14)-C(15)	112.2(6)
C(22)-C(17)-C(18)	118.7(7)
C(19)-C(18)-C(17)	122.0(8)
C(20)-C(19)-C(18)	117.5(7)
C(20)-C(19)-C(14)	120.8(6)
C(18)-C(19)-C(14)	121.7(8)
C(21)-C(20)-C(19)	120.8(7)
C(22)-C(21)-C(20)	121.7(8)
C(21)-C(22)-O(3)	119.5(8)
C(21)-C(22)-C(17)	119.1(7)
O(3)-C(22)-C(17)	121.3(7)
C(24)-C(23)-C(28)	122.1(7)
C(25)-C(24)-C(23)	118.9(7)
C(24)-C(25)-C(26)	121.2(7)
C(24)-C(25)-O(3)	123.1(7)
C(26)-C(25)-O(3)	115.4(7)
C(27)-C(26)-C(25)	118.9(7)
C(26)-C(27)-C(28)	121.9(7)
C(23)-C(28)-C(27)	117.0(7)
C(23)-C(28)-C(1)#1	125.0(7)
C(27)-C(28)-C(1)#1	117.9(6)
Cl(1)-C(30)-Cl(2)	109.47(9)
Cl(1)-C(30)-Cl(3)	109.45(9)
Cl(2)-C(30)-Cl(3)	109.47(9)

Anisotropic Displacement Parameters-U's

	U11	U22	U33	U23	U13	U12
O (1)	41 (3)	41 (3)	61 (4)	7 (3)	-4 (3)	6 (3)
O (2)	21 (3)	57 (3)	54 (4)	22 (3)	0 (3)	-1 (2)
O (3)	82 (4)	22 (3)	42 (4)	4 (3)	-12 (3)	-10 (3)
C (1)	28 (4)	25 (4)	38 (5)	-6 (4)	-1 (4)	0 (3)
C (2)	44 (5)	38 (4)	26 (5)	13 (4)	-8 (4)	2 (4)
C (3)	31 (4)	32 (4)	44 (6)	3 (4)	-2 (4)	-4 (3)
C (4)	20 (4)	23 (4)	57 (6)	-1 (4)	-4 (4)	5 (3)
C (5)	27 (4)	34 (4)	56 (7)	4 (4)	-15 (4)	2 (3)
C (6)	37 (5)	38 (4)	31 (5)	2 (4)	-6 (4)	-2 (4)
C (7)	34 (5)	27 (4)	41 (6)	-7 (4)	-1 (4)	-1 (3)
C (8)	37 (5)	29 (4)	61 (7)	-18 (4)	-3 (5)	5 (3)
C (9)	41 (5)	31 (4)	60 (7)	-11 (4)	-22 (5)	-1 (3)
C (10)	21 (4)	40 (4)	35 (6)	16 (4)	6 (4)	8 (3)
C (11)	34 (5)	34 (4)	69 (7)	1 (4)	4 (5)	4 (4)
C (12)	34 (5)	27 (4)	47 (6)	-9 (4)	-9 (4)	-1 (3)
C (13)	30 (4)	28 (4)	34 (5)	6 (4)	-1 (4)	-1 (3)
C (14)	26 (4)	32 (4)	47 (6)	1 (4)	0 (4)	4 (3)
C (15)	30 (4)	31 (4)	54 (6)	8 (4)	-1 (4)	1 (3)
C (16)	38 (4)	28 (4)	43 (6)	-3 (4)	-7 (4)	-1 (3)
C (17)	43 (5)	24 (4)	41 (6)	-2 (4)	-8 (4)	2 (3)
C (18)	41 (5)	35 (4)	34 (6)	-4 (4)	6 (4)	2 (3)
C (19)	30 (4)	26 (4)	30 (6)	-6 (4)	-2 (4)	-3 (3)
C (20)	44 (5)	30 (4)	37 (6)	6 (4)	7 (4)	5 (3)
C (21)	54 (5)	35 (5)	34 (6)	5 (4)	5 (4)	3 (4)
C (22)	48 (5)	27 (4)	35 (6)	13 (4)	-6 (4)	-8 (3)
C (23)	36 (4)	29 (4)	49 (6)	7 (4)	0 (4)	2 (3)
C (24)	41 (5)	27 (4)	70 (7)	-4 (4)	-3 (5)	14 (3)
C (25)	46 (5)	30 (4)	38 (6)	5 (4)	1 (4)	-6 (4)
C (26)	31 (4)	38 (4)	42 (6)	-5 (4)	7 (4)	-5 (3)
C (27)	28 (4)	30 (4)	42 (6)	0 (4)	4 (4)	3 (3)
C (28)	24 (4)	29 (4)	42 (6)	5 (4)	5 (4)	1 (3)
C (30)	685 (69)	79 (13)	364 (38)	-54 (20)	-376 (46)	-16 (26)
Cl (1)	172 (6)	350 (10)	401 (13)	119 (10)	73 (7)	45 (6)
Cl (2)	193 (6)	231 (7)	490 (15)	116 (9)	60 (8)	74 (5)
Cl (3)	313 (9)	200 (6)	220 (6)	-14 (5)	-86 (6)	24 (5)

Coordinates of hydrogen atoms ($\times 10^3$)

	x	y	z	U (eq)
H (2A)	2237 (5)	5852 (2)	-1890 (7)	43
H (3A)	3595 (5)	6043 (2)	-2529 (8)	43
H (5A)	4572 (4)	5424 (2)	449 (8)	47
H (6A)	3225 (5)	5247 (2)	1163 (7)	42
H (8A)	-301 (5)	6306 (2)	-632 (8)	51
H (9A)	960 (5)	6132 (2)	280 (8)	53
H (11A)	965 (5)	4918 (3)	-1437 (8)	55
H (12A)	-310 (5)	5095 (2)	-2363 (7)	43
H (15A)	-1808 (5)	5979 (2)	-289 (7)	58
H (15B)	-1920 (5)	5457 (2)	-604 (7)	58
H (15C)	-2544 (5)	5820 (2)	-1183 (7)	58
H (16A)	-2218 (5)	5548 (2)	-3300 (7)	54
H (16B)	-1663 (5)	5170 (2)	-2644 (7)	54
H (16C)	-1265 (5)	5473 (2)	-3706 (7)	54
H (17A)	-1656 (5)	7373 (2)	-1807 (8)	43
H (18A)	-1695 (5)	6631 (2)	-1019 (8)	44
H (20A)	-1088 (5)	6138 (2)	-4343 (8)	44
H (21A)	-1038 (5)	6867 (3)	-5118 (8)	49
H (23A)	633 (5)	8336 (2)	-1865 (7)	46
H (24A)	109 (5)	7691 (2)	-2828 (8)	55
H (26A)	-1991 (5)	8390 (2)	-3785 (7)	44
H (27A)	-1476 (4)	9022 (2)	-2796 (7)	40
H (30A)	1491 (4)	6481 (2)	-4681 (6)	451

Appendix B: The Crystal Structure Data of Macrocycle 3.16 (n=2)

Coordinates and Equivalent Isotropic Thermal Parameters

Atom	<u>x</u>	<u>y</u>	<u>z</u>	<u>B_{eq}</u> (Å ²)
O1A	0.6167(2)	0.3548(2)	0.9726(2)	5.76(6)
O2A	0.1424(2)	0.4452(2)	0.8896(2)	6.46(7)
O3A	0.1406(2)	0.4304(2)	0.4544(2)	5.51(6)
O4A	0.4726(2)	0.3515(2)	0.2127(1)	5.19(6)
O5A	0.9438(2)	0.2532(2)	0.2953(2)	6.08(6)
O6A	0.9472(2)	0.2702(2)	0.7309(2)	5.36(6)
C1A	0.5205(3)	0.3743(2)	0.9356(2)	4.32(8)
C2A	0.4290(3)	0.3580(2)	0.9849(2)	4.65(8)
C3A	0.3308(3)	0.3750(2)	0.9516(2)	4.60(8)
C4A	0.3215(2)	0.4080(2)	0.8675(2)	4.07(8)
C5A	0.4156(3)	0.4280(2)	0.8213(2)	4.84(8)
C6A	0.5148(3)	0.4118(2)	0.8545(2)	4.79(8)
C7A	0.2132(3)	0.4255(2)	0.8340(2)	4.68(8)
C8A	0.1930(2)	0.4203(2)	0.7330(2)	4.23(8)
C9A	0.1143(3)	0.4719(2)	0.7028(2)	4.56(8)
C10A	0.0977(3)	0.4743(2)	0.6107(2)	4.54(8)
C11A	0.1594(3)	0.4242(2)	0.5466(2)	4.57(8)
C12A	0.2328(3)	0.3674(3)	0.5727(2)	5.21(9)
C13A	0.2496(3)	0.3662(3)	0.6657(2)	5.08(9)
C14A	0.2252(3)	0.4122(2)	0.3939(2)	4.61(8)
C15A	0.2075(3)	0.3439(3)	0.3172(2)	5.29(9)
C16A	0.2907(3)	0.3242(3)	0.2569(2)	5.20(9)
C17A	0.3895(3)	0.3732(2)	0.2742(2)	4.31(8)
C18A	0.4064(3)	0.4443(2)	0.3489(2)	4.84(8)
C19A	0.3230(3)	0.4633(2)	0.4092(2)	5.04(9)
C20A	0.5673(2)	0.3274(2)	0.2488(2)	4.11(8)
C21A	0.5702(2)	0.2892(2)	0.3292(2)	4.46(8)
C22A	0.6677(3)	0.2685(2)	0.3610(2)	4.46(8)
C23A	0.7620(2)	0.2849(2)	0.3148(2)	4.15(8)
C24A	0.7542(3)	0.3176(2)	0.2310(2)	4.58(8)
C25A	0.6580(3)	0.3391(2)	0.1978(2)	4.66(8)
C26A	0.8698(3)	0.2692(2)	0.3497(2)	4.58(8)
C27A	0.8900(2)	0.2739(2)	0.4506(2)	4.19(8)
C28A	0.9718(3)	0.2260(2)	0.4811(2)	4.46(8)
C29A	0.9897(3)	0.2254(2)	0.5734(2)	4.66(8)
C30A	0.9268(2)	0.2744(2)	0.6388(2)	4.33(8)
C31A	0.8488(3)	0.3278(2)	0.6109(2)	4.95(9)
C32A	0.8311(3)	0.3264(2)	0.5171(2)	4.74(8)
C33A	0.8637(3)	0.2908(2)	0.7928(2)	4.57(8)
C34A	0.7741(3)	0.2296(3)	0.7896(3)	5.7(1)
C35A	0.6915(3)	0.2510(3)	0.8498(3)	5.7(1)
C36A	0.7002(3)	0.3330(2)	0.9112(2)	4.60(8)
C37A	0.7915(3)	0.3928(3)	0.9163(2)	5.41(9)
C38A	0.8744(3)	0.3716(3)	0.8567(2)	5.37(9)
O1B	-0.4182(2)	-0.0884(2)	0.1368(2)	6.01(6)
O2B	-0.4232(2)	-0.0737(2)	-0.2930(2)	6.90(7)
O3B	0.0669(2)	0.0149(2)	-0.3764(1)	5.09(6)
C1B	-0.3982(3)	-0.0761(2)	0.0461(2)	4.63(8)
C2B	-0.4683(3)	-0.1246(2)	-0.0210(2)	4.89(8)
C3B	-0.4513(3)	-0.1166(2)	-0.1117(2)	4.72(8)

Atom	x	y	z	B _{eq} (Å ²)
----	-	-	-	-----
C4B	-0.3649(2)	-0.0614(2)	-0.1381(2)	4.38(8)
C5B	-0.2985(3)	-0.0093(2)	-0.0684(2)	4.90(8)
C6B	-0.3147(3)	-0.0163(3)	0.0234(2)	5.09(9)
C7B	-0.3469(3)	-0.0595(2)	-0.2381(2)	4.89(9)
C8B	-0.2356(3)	-0.0430(2)	-0.2715(2)	4.33(8)
C9B	-0.2214(3)	-0.0093(2)	-0.3553(2)	4.62(8)
C10B	-0.1204(3)	0.0090(2)	-0.3889(2)	4.65(8)
C11B	-0.0315(3)	-0.0058(2)	-0.3391(2)	4.19(8)
C12B	-0.0434(3)	-0.0438(2)	-0.2592(2)	4.74(8)
C13B	-0.1453(3)	-0.0625(2)	-0.2261(2)	4.89(8)
C14B	0.1552(3)	0.0343(2)	-0.3153(2)	4.42(8)
C15B	0.1587(3)	0.1104(3)	-0.2448(3)	5.39(9)
C16B	0.2462(3)	0.1286(3)	-0.1848(3)	5.59(9)
C17B	0.3293(3)	0.0707(2)	-0.1975(2)	4.80(8)
C18B	0.3277(3)	-0.0033(3)	-0.2696(3)	5.36(9)
C19B	0.2394(3)	-0.0212(2)	-0.3289(2)	5.05(9)
O1S	0.1365(3)	0.2139(3)	0.0516(3)	13.1(1)
C1S	0.0456(4)	0.2444(4)	0.0508(3)	9.6(1)
C2S	0.0364(4)	0.3466(3)	0.0846(4)	9.9(2)
C3S	-0.0524(5)	0.1765(5)	0.0232(5)	15.0(2)
O2S	0.4991(4)	0.2872(4)	0.5621(3)	16.7(2)
C4S	0.5046(7)	0.1944(4)	0.5754(4)	20.1(3)
C5S	0.4000(6)	0.1435(5)	0.5312(5)	17.7(3)
C61S	0.5359(9)	0.195(1)	0.6589(6)	13.6(4)*
C62S	0.605(1)	0.1379(7)	0.5439(8)	13.1(4)*

* C61S and C62S are half-populated.

$$B_{eq} = (8\pi^2/3) \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

Anisotropic Displacement Parameters - U's

Name	U(1,1)	U(2,2)	U(3,3)	U(1,2)	U(1,3)	U(2,3)
O1A	0.058(1)	0.117(2)	0.049(1)	0.026(1)	0.001(1)	0.018(1)
O2A	0.052(1)	0.133(2)	0.058(1)	0.016(1)	0.008(1)	0.007(2)
O3A	0.050(1)	0.110(2)	0.055(1)	0.027(1)	0.004(1)	0.022(1)
O4A	0.053(1)	0.100(2)	0.048(1)	0.019(1)	0.003(1)	0.015(1)
O5A	0.055(1)	0.111(2)	0.067(2)	0.024(1)	0.009(1)	0.011(1)
O6A	0.052(1)	0.097(2)	0.059(1)	0.024(1)	0.003(1)	0.017(1)
C1A	0.050(2)	0.067(2)	0.048(2)	0.010(2)	-0.003(2)	0.008(2)
C2A	0.062(2)	0.072(2)	0.045(2)	0.013(2)	0.008(2)	0.013(2)
C3A	0.055(2)	0.072(2)	0.048(2)	0.004(2)	0.011(2)	0.010(2)
C4A	0.046(2)	0.058(2)	0.050(2)	0.002(2)	0.001(2)	0.007(2)
C5A	0.053(2)	0.076(2)	0.059(2)	0.006(2)	0.003(2)	0.024(2)
C6A	0.049(2)	0.082(2)	0.055(2)	0.006(2)	0.006(2)	0.024(2)
C7A	0.047(2)	0.071(2)	0.058(2)	0.002(2)	0.004(2)	0.006(2)
C8A	0.044(2)	0.064(2)	0.052(2)	0.005(2)	0.001(2)	0.007(2)
C9A	0.044(2)	0.065(2)	0.062(2)	0.008(2)	0.007(2)	0.004(2)
C10A	0.043(2)	0.067(2)	0.065(2)	0.010(2)	0.002(2)	0.014(2)
C11A	0.044(2)	0.076(2)	0.055(2)	0.011(2)	0.000(2)	0.013(2)
C12A	0.065(2)	0.087(2)	0.049(2)	0.030(2)	0.002(2)	0.008(2)
C13A	0.057(2)	0.081(2)	0.058(2)	0.025(2)	-0.001(2)	0.011(2)
C14A	0.045(2)	0.081(2)	0.055(2)	0.018(2)	0.002(2)	0.020(2)
C15A	0.046(2)	0.091(3)	0.063(2)	0.003(2)	-0.006(2)	0.011(2)
C16A	0.056(2)	0.086(2)	0.054(2)	0.009(2)	-0.005(2)	0.005(2)
C17A	0.049(2)	0.071(2)	0.047(2)	0.011(2)	0.000(2)	0.014(2)
C18A	0.049(2)	0.066(2)	0.069(2)	0.004(2)	0.003(2)	0.011(2)
C19A	0.057(2)	0.069(2)	0.064(2)	0.014(2)	0.002(2)	0.005(2)
C20A	0.048(2)	0.062(2)	0.045(2)	0.008(2)	0.002(2)	0.006(2)
C21A	0.042(2)	0.075(2)	0.055(2)	0.003(2)	0.005(2)	0.019(2)
C22A	0.053(2)	0.065(2)	0.054(2)	0.007(2)	0.003(2)	0.020(2)
C23A	0.047(2)	0.056(2)	0.054(2)	0.006(2)	0.004(2)	0.006(2)
C24A	0.050(2)	0.072(2)	0.051(2)	0.007(2)	0.011(2)	0.006(2)
C25A	0.054(2)	0.076(2)	0.047(2)	0.006(2)	0.005(2)	0.011(2)
C26A	0.051(2)	0.060(2)	0.063(2)	0.010(2)	0.006(2)	0.006(2)
C27A	0.046(2)	0.054(2)	0.059(2)	0.009(2)	0.006(2)	0.005(2)
C28A	0.047(2)	0.058(2)	0.065(2)	0.012(2)	0.006(2)	0.009(2)
C29A	0.049(2)	0.061(2)	0.070(2)	0.015(2)	0.003(2)	0.015(2)
C30A	0.045(2)	0.058(2)	0.062(2)	0.008(2)	0.000(2)	0.009(2)
C31A	0.055(2)	0.067(2)	0.065(2)	0.019(2)	-0.001(2)	0.002(2)
C32A	0.057(2)	0.064(2)	0.060(2)	0.018(2)	-0.004(2)	0.007(2)
C33A	0.047(2)	0.072(2)	0.057(2)	0.014(2)	0.001(2)	0.012(2)
C34A	0.070(2)	0.064(2)	0.078(2)	0.001(2)	0.011(2)	0.001(2)
C35A	0.062(2)	0.074(2)	0.077(2)	-0.003(2)	0.010(2)	0.008(2)
C36A	0.052(2)	0.076(2)	0.050(2)	0.016(2)	-0.000(2)	0.015(2)
C37A	0.064(2)	0.081(2)	0.056(2)	0.010(2)	-0.003(2)	-0.004(2)
C38A	0.053(2)	0.081(2)	0.067(2)	0.001(2)	-0.005(2)	0.006(2)
O1B	0.050(1)	0.115(2)	0.065(1)	-0.000(1)	-0.002(1)	0.026(1)
O2B	0.055(1)	0.135(2)	0.070(2)	-0.001(2)	-0.008(1)	0.014(2)
O3B	0.050(1)	0.094(2)	0.051(1)	0.006(1)	0.004(1)	0.015(1)
C1B	0.046(2)	0.073(2)	0.058(2)	0.006(2)	0.003(2)	0.016(2)
C2B	0.046(2)	0.069(2)	0.073(2)	0.002(2)	0.003(2)	0.018(2)
C3B	0.051(2)	0.063(2)	0.063(2)	0.003(2)	-0.006(2)	0.005(2)

Name	U(1,1)	U(2,2)	U(3,3)	U(1,2)	U(1,3)	U(2,3)
C4B	0.044(2)	0.064(2)	0.058(2)	0.004(2)	0.003(2)	0.009(2)
C5B	0.051(2)	0.071(2)	0.065(2)	-0.001(2)	0.002(2)	0.013(2)
C6B	0.053(2)	0.080(2)	0.057(2)	-0.005(2)	-0.001(2)	0.006(2)
C7B	0.049(2)	0.070(2)	0.066(2)	0.005(2)	-0.003(2)	0.008(2)
C8B	0.054(2)	0.059(2)	0.050(2)	0.004(2)	-0.002(2)	0.007(2)
C9B	0.055(2)	0.067(2)	0.052(2)	0.004(2)	-0.011(2)	0.007(2)
C10B	0.057(2)	0.070(2)	0.049(2)	-0.001(2)	-0.004(2)	0.010(2)
C11B	0.048(2)	0.060(2)	0.051(2)	0.008(2)	0.005(2)	0.006(2)
C12B	0.051(2)	0.078(2)	0.057(2)	0.018(2)	0.003(2)	0.022(2)
C13B	0.055(2)	0.077(2)	0.060(2)	0.014(2)	0.003(2)	0.025(2)
C14B	0.050(2)	0.069(2)	0.050(2)	0.005(2)	0.005(2)	0.011(2)
C15B	0.064(2)	0.074(2)	0.067(2)	0.023(2)	-0.000(2)	0.004(2)
C16B	0.067(2)	0.076(2)	0.066(2)	0.013(2)	-0.008(2)	-0.002(2)
C17B	0.046(2)	0.082(2)	0.057(2)	0.005(2)	-0.000(2)	0.020(2)
C18B	0.051(2)	0.082(2)	0.074(2)	0.020(2)	0.007(2)	0.015(2)
C19B	0.056(2)	0.071(2)	0.064(2)	0.009(2)	0.009(2)	0.007(2)
O1S	0.157(3)	0.146(3)	0.202(4)	0.042(3)	0.019(3)	0.034(3)
C1S	0.094(3)	0.173(4)	0.112(3)	0.031(3)	0.015(3)	0.055(3)
C2S	0.129(4)	0.107(3)	0.146(4)	0.039(3)	0.044(3)	0.022(3)
C3S	0.163(5)	0.168(5)	0.223(6)	-0.045(5)	-0.076(5)	0.016(5)
O2S	0.183(4)	0.238(5)	0.198(4)	0.011(4)	0.068(3)	-0.015(4)
C4S	0.426(9)	0.142(5)	0.170(5)	-0.109(5)	0.117(5)	0.018(4)
C5S	0.257(7)	0.196(6)	0.180(6)	-0.115(5)	-0.032(6)	-0.016(5)
C61S	0.18(1)	0.28(1)	0.066(5)	0.031(9)	-0.052(6)	0.049(7)
C62S	0.22(1)	0.138(7)	0.164(9)	0.095(7)	0.009(9)	0.062(6)

The form of the anisotropic displacement factor is:

$$\exp[-2\pi^2\{h^2a^2U_{11}+k^2b^2U_{22}+l^2c^2U_{33}+2(hka^*b^*U_{12}+hla^*c^*U_{13}+klb^*c^*U_{23})\}]$$

Table of Bond Distances in Angstroms

Atom 1	Atom 2	Distance	Atom 1	Atom 2	Distance
O1A	C1A	1.385(4)	C14A	C19A	1.370(4)
O1A	C36A	1.399(4)	C15A	C16A	1.384(5)
O2A	C7A	1.222(4)	C16A	C17A	1.370(4)
O3A	C11A	1.387(4)	C17A	C18A	1.375(4)
O3A	C14A	1.393(4)	C18A	C19A	1.383(5)
O4A	C17A	1.397(4)	C20A	C21A	1.379(5)
O4A	C20A	1.386(4)	C20A	C25A	1.372(4)
O5A	C26A	1.232(4)	C21A	C22A	1.373(5)
O6A	C30A	1.382(4)	C22A	C23A	1.381(4)
O6A	C33A	1.401(4)	C23A	C24A	1.390(5)
C1A	C2A	1.377(5)	C23A	C26A	1.486(5)
C1A	C6A	1.385(5)	C24A	C25A	1.372(5)
C2A	C3A	1.373(5)	C26A	C27A	1.487(5)
C3A	C4A	1.397(5)	C27A	C28A	1.390(5)
C4A	C5A	1.389(4)	C27A	C32A	1.386(4)
C4A	C7A	1.492(5)	C28A	C29A	1.369(5)
C5A	C6A	1.380(5)	C29A	C30A	1.383(4)
C7A	C8A	1.487(5)	C30A	C31A	1.390(5)
C8A	C9A	1.394(5)	C31A	C32A	1.387(5)
C8A	C13A	1.387(4)	C33A	C34A	1.362(5)
C9A	C10A	1.369(5)	C33A	C38A	1.367(5)
C10A	C11A	1.370(4)	C34A	C35A	1.381(5)
C11A	C12A	1.372(5)	C35A	C36A	1.361(5)
C12A	C13A	1.379(5)	C36A	C37A	1.365(5)
C14A	C15A	1.372(4)	C37A	C38A	1.377(5)

Table of Bond Angles in Degrees

Atom 1	Atom 2	Atom 3	Angle	Atom 1	Atom 2	Atom 3	Angle
C1A	O1A	C36A	117.6(2)	C11A	C12A	C13A	119.1(3)
C11A	O3A	C14A	116.7(2)	C8A	C13A	C12A	121.4(3)
C17A	O4A	C20A	117.6(2)	O3A	C14A	C15A	118.6(3)
C30A	O6A	C33A	116.7(2)	O3A	C14A	C19A	120.7(3)
O1A	C1A	C2A	117.0(3)	C15A	C14A	C19A	120.7(3)
O1A	C1A	C6A	122.6(3)	C14A	C15A	C16A	119.4(3)
C2A	C1A	C6A	120.3(3)	C15A	C16A	C17A	119.7(3)
C1A	C2A	C3A	119.9(3)	O4A	C17A	C16A	118.7(3)
C2A	C3A	C4A	121.1(3)	O4A	C17A	C18A	120.2(3)
C3A	C4A	C5A	117.7(3)	C16A	C17A	C18A	121.0(3)
C3A	C4A	C7A	119.3(3)	C17A	C18A	C19A	118.9(3)
C5A	C4A	C7A	122.9(3)	C14A	C19A	C18A	120.1(3)
C4A	C5A	C6A	121.6(3)	O4A	C20A	C21A	122.4(3)
C1A	C6A	C5A	119.2(3)	O4A	C20A	C25A	116.3(3)
O2A	C7A	C4A	119.9(3)	C21A	C20A	C25A	121.2(3)
O2A	C7A	C8A	120.7(3)	C20A	C21A	C22A	118.6(3)
C4A	C7A	C8A	119.4(3)	C21A	C22A	C23A	121.9(3)
C7A	C8A	C9A	119.5(3)	C22A	C23A	C24A	117.4(3)
C7A	C8A	C13A	123.1(3)	C22A	C23A	C26A	123.7(3)
C9A	C8A	C13A	117.3(3)	C24A	C23A	C26A	118.9(3)
C8A	C9A	C10A	121.7(3)	C23A	C24A	C25A	121.7(3)
C9A	C10A	C11A	119.2(3)	C20A	C25A	C24A	118.8(3)
O3A	C11A	C10A	116.8(3)	O5A	C26A	C23A	120.3(3)
O3A	C11A	C12A	122.0(3)	O5A	C26A	C27A	119.3(3)
C10A	C11A	C12A	121.1(3)	C23A	C26A	C27A	120.4(3)

Bond Distances (cont.)

Atom 1 -----	Atom 2 -----	Distance -----	Atom 1 -----	Atom 2 -----	Distance -----
O1B	C1B	1.388(4)	C10B	C11B	1.376(5)
O1B	C17B	1.399(4)	C11B	C12B	1.373(5)
O2B	C7B	1.226(4)	C12B	C13B	1.383(5)
O3B	C11B	1.376(4)	C14B	C15B	1.377(4)
O3B	C14B	1.397(4)	C14B	C19B	1.370(5)
C1B	C2B	1.374(4)	C15B	C16B	1.379(5)
C1B	C6B	1.373(5)	C16B	C17B	1.381(5)
C2B	C3B	1.365(5)	C17B	C18B	1.372(5)
C3B	C4B	1.380(5)	C18B	C19B	1.381(5)
C4B	C5B	1.391(4)	O1S	C1S	1.252(6)
C4B	C7B	1.485(5)	C1S	C2S	1.491(7)
C5B	C6B	1.376(5)	C1S	C3S	1.513(8)
C7B	C8B	1.487(5)	O2S	C4S	1.391(8)
C8B	C9B	1.397(5)	C4S	C5S	1.53(1)
C8B	C13B	1.378(5)	C4S	C61S	1.28(1)
C9B	C10B	1.375(5)	C4S	C62S	1.58(1)

Bond Angles (cont.)

Atom 1	Atom 2	Atom 3	Angle	Atom 1	Atom 2	Atom 3	Angle
=====	=====	=====	=====	=====	=====	=====	=====
C26A	C27A	C28A	120.0(3)	C1B	C2B	C3B	119.4(3)
C26A	C27A	C32A	122.2(3)	C2B	C3B	C4B	121.8(3)
C28A	C27A	C32A	117.7(3)	C3B	C4B	C5B	117.5(3)
C27A	C28A	C29A	121.6(3)	C3B	C4B	C7B	119.5(3)
C28A	C29A	C30A	120.0(3)	C5B	C4B	C7B	123.0(3)
O6A	C30A	C29A	117.6(3)	C4B	C5B	C6B	121.4(3)
O6A	C30A	C31A	122.6(3)	C1B	C6B	C5B	119.0(3)
C29A	C30A	C31A	119.8(3)	O2B	C7B	C4B	120.0(3)
C30A	C31A	C32A	119.2(3)	O2B	C7B	C8B	120.4(3)
C27A	C32A	C31A	121.5(3)	C4B	C7B	C8B	119.6(3)
O6A	C33A	C34A	119.7(3)	C7B	C8B	C9B	118.5(3)
O6A	C33A	C38A	119.4(3)	C7B	C8B	C13B	123.7(3)
C34A	C33A	C38A	120.9(3)	C9B	C8B	C13B	117.8(3)
C33A	C34A	C35A	119.4(3)	C8B	C9B	C10B	121.2(3)
C34A	C35A	C36A	119.8(3)	C9B	C10B	C11B	119.5(3)
O1A	C36A	C35A	119.9(3)	O3B	C11B	C10B	116.3(3)
O1A	C36A	C37A	119.3(3)	O3B	C11B	C12B	123.2(3)
C35A	C36A	C37A	120.7(3)	C10B	C11B	C12B	120.4(3)
C36A	C37A	C38A	119.7(3)	C11B	C12B	C13B	119.7(3)
C33A	C38A	C37A	119.4(3)	C8B	C13B	C12B	121.2(3)
C1B	O1B	C17B	115.8(2)	O3B	C14B	C15B	120.1(3)
C11B	O3B	C14B	117.0(2)	O3B	C14B	C19B	119.0(3)
O1B	C1B	C2B	116.9(3)	C15B	C14B	C19B	120.8(3)
O1B	C1B	C6B	122.4(3)	C14B	C15B	C16B	119.5(3)
C2B	C1B	C6B	120.7(3)	C15B	C16B	C17B	119.2(3)

Bond Angles (cont.)

Atom 1 =====	Atom 2 =====	Atom 3 =====	Angle =====	Atom 1 =====	Atom 2 =====	Atom 3 =====	Angle =====
O1B	C17B	C16B	119.6(3)	C2S	C1S	C3S	121.7(5)
O1B	C17B	C18B	119.0(3)	O2S	C4S	C5S	103.8(6)
C16B	C17B	C18B	121.4(3)	O2S	C4S	C61S	108.4(8)
C17B	C18B	C19B	118.9(3)	O2S	C4S	C62S	121.8(7)
C14B	C19B	C18B	120.1(3)	C5S	C4S	C61S	125.2(8)
O1S	C1S	C2S	118.4(4)	C5S	C4S	C62S	111.6(6)
O1S	C1S	C3S	119.7(5)	C61S	C4S	C62S	87.0(8)

Coordinates Assigned to Hydrogen Atoms

Atom	x	y	z	B _{iso} (Å ²)
----	-	-	-	-----
H2A	0.4338	0.3350	1.0419	6
H3A	0.2680	0.3642	0.9863	5
H5A	0.4115	0.4534	0.7655	6
H6A	0.5783	0.4261	0.8221	6
H9A	0.0710	0.5062	0.7473	5
H10A	0.0439	0.5103	0.5915	5
H12A	0.2714	0.3293	0.5272	6
H13A	0.3010	0.3275	0.6840	6
H15A	0.1386	0.3103	0.3056	6
H16A	0.2794	0.2768	0.2036	6
H18A	0.4741	0.4798	0.3588	6
H19A	0.3335	0.5119	0.4614	6
H21A	0.5062	0.2773	0.3619	5
H22A	0.6702	0.2421	0.4162	5
H24A	0.8171	0.3252	0.1957	5
H25A	0.6542	0.3617	0.1404	6
H28A	1.0163	0.1929	0.4368	5
H29A	1.0454	0.1913	0.5923	6
H31A	0.8081	0.3646	0.6555	6
H32A	0.7772	0.3622	0.4978	6
H34A	0.7684	0.1726	0.7462	7
H35A	0.6287	0.2085	0.8484	7
H37A	0.7978	0.4489	0.9608	7
H38A	0.9383	0.4127	0.8598	6
H2B	-0.5280	-0.1632	-0.0044	6
H3B	-0.5002	-0.1499	-0.1577	6
H5B	-0.2407	0.0319	-0.0843	6
H6B	-0.2686	0.0196	0.0703	6
H9B	-0.2826	0.0012	-0.3896	6
H10B	-0.1120	0.0317	-0.4461	6
H12B	0.0180	-0.0571	-0.2267	6
H13B	-0.1531	-0.0892	-0.1710	6
H15B	0.1013	0.1501	-0.2376	7
H16B	0.2491	0.1804	-0.1353	7
H18B	0.3863	-0.0414	-0.2785	6
H19B	0.2370	-0.0721	-0.3791	6

Appendix C: X-ray Structure Data of Macrocycle 3.16 (n=3)Coordinates ($\times 10^{-4}$) and Equivalent Isotropic Thermal Parameters ($\times 10^{-3}$)

	x	y	z	U (eq)
O (1)	15425 (2)	3937 (1)	2589 (1)	67 (1)
O (2)	15559 (2)	6890 (2)	-608 (1)	92 (1)
O (3)	11953 (2)	9417 (1)	-2086 (1)	67 (1)
O (4)	10813 (3)	13317 (1)	-2737 (1)	84 (1)
O (5)	9774 (2)	13820 (1)	755 (1)	63 (1)
O (6)	9820 (2)	11784 (1)	3882 (1)	64 (1)
O (7)	5976 (3)	8989 (2)	6224 (1)	94 (1)
O (8)	5230 (2)	6386 (1)	4433 (1)	57 (1)
O (9)	9145 (2)	3772 (1)	4278 (1)	50 (1)
C (1)	14415 (3)	4382 (2)	2351 (2)	49 (1)
C (2)	16128 (3)	6101 (2)	652 (2)	78 (1)
C (3)	15865 (3)	5474 (2)	1367 (2)	66 (1)
C (4)	14631 (3)	5066 (2)	1573 (2)	50 (1)
C (5)	13668 (3)	5283 (2)	1033 (2)	57 (1)
C (6)	13939 (3)	5897 (2)	304 (2)	66 (1)
C (7)	15164 (3)	6305 (2)	127 (2)	67 (1)
C (8)	12722 (3)	8541 (2)	-848 (2)	62 (1)
C (9)	13591 (3)	7888 (2)	-475 (2)	68 (1)
C (10)	14589 (3)	7520 (2)	-936 (2)	61 (1)
C (11)	14758 (3)	7805 (2)	-1762 (2)	63 (1)
C (12)	13909 (3)	8468 (2)	-2136 (2)	58 (1)
C (13)	12898 (3)	8823 (2)	-1675 (2)	52 (1)
C (14)	12248 (3)	11390 (2)	-1620 (2)	63 (1)
C (15)	12531 (3)	10563 (2)	-1623 (2)	60 (1)
C (16)	11821 (3)	10235 (2)	-2059 (2)	50 (1)
C (17)	10879 (3)	10737 (2)	-2533 (2)	57 (1)
C (18)	10636 (3)	11567 (2)	-2548 (2)	56 (1)
C (19)	11283 (3)	11897 (2)	-2072 (2)	52 (1)
C (20)	10927 (3)	12793 (2)	-2092 (2)	57 (1)
C (21)	10108 (3)	12682 (2)	135 (2)	59 (1)
C (22)	10397 (3)	12447 (2)	-570 (2)	60 (1)
C (23)	10650 (3)	13030 (2)	-1324 (2)	50 (1)
C (24)	10554 (3)	13875 (2)	-1350 (2)	50 (1)
C (25)	10254 (3)	14119 (2)	-652 (2)	50 (1)
C (26)	10047 (3)	13520 (2)	89 (2)	48 (1)
C (27)	10981 (3)	12298 (2)	2538 (2)	57 (1)
C (28)	10999 (3)	12821 (2)	1761 (2)	59 (1)
C (29)	9784 (3)	13257 (2)	1531 (2)	51 (1)
C (30)	8566 (3)	13200 (2)	2065 (2)	55 (1)
C (31)	8554 (3)	12696 (2)	2849 (2)	55 (1)
C (32)	9753 (3)	12248 (2)	3080 (2)	51 (1)
C (33)	7535 (3)	10062 (1)	4209 (2)	44 (1)
C (34)	8342 (3)	10737 (2)	3804 (2)	44 (1)
C (35)	8949 (3)	11134 (2)	4240 (2)	47 (1)
C (36)	8740 (3)	10866 (2)	5076 (2)	57 (1)
C (37)	7943 (3)	10194 (2)	5473 (2)	55 (1)
C (38)	7328 (3)	9774 (2)	5051 (1)	44 (1)
C (39)	6444 (3)	9065 (2)	5508 (2)	54 (1)

C(40)	6837(3)	7436(2)	4356(2)	47(1)
C(41)	7102(3)	8116(2)	4596(2)	45(1)
C(42)	6130(3)	8420(2)	5138(2)	45(1)
C(43)	4858(3)	8043(2)	5414(2)	52(1)
C(44)	4569(3)	7373(2)	5169(2)	53(1)
C(45)	5579(3)	7064(2)	4657(2)	47(1)
C(46)	7226(3)	4688(2)	3770(2)	49(1)
C(47)	6264(3)	5347(2)	3813(2)	50(1)
C(48)	6249(2)	5740(2)	4406(2)	44(1)
C(49)	7140(3)	5468(2)	4969(2)	49(1)
C(50)	8114(3)	4808(2)	4921(2)	47(1)
C(51)	8156(2)	4438(1)	4315(2)	42(1)
C(52)	11967(3)	4894(2)	2797(2)	45(1)
C(53)	10678(3)	4766(1)	3283(2)	44(1)
C(54)	10419(2)	3974(1)	3796(1)	40(1)
C(55)	11431(3)	3330(1)	3845(1)	41(1)
C(56)	12717(3)	3469(2)	3374(1)	42(1)
C(57)	13000(2)	4250(1)	2834(1)	41(1)
O(61)	8361(10)	9915(8)	-780(5)	324(5)
C(61)	8090(12)	9499(7)	-1405(9)	267(6)
C(62)	6446(17)	9692(15)	-1335(10)	452(18)
C(63)	6587(18)	9199(10)	-737(12)	378(12)
C(64)	7087(11)	9865(8)	-390(5)	252(6)
O(65)	2787(9)	6998(4)	2960(9)	270(4)
C(65)	2728(12)	7795(11)	3291(8)	275(7)
C(66)	4063(26)	7937(14)	2825(10)	390(17)
C(67)	4270(12)	7911(9)	2096(14)	334(11)
C(68)	3262(18)	7305(10)	2048(9)	290(7)

Bond Length (Å)

O(1)-C(1)	1.226(3)
O(2)-C(7)	1.389(3)
O(2)-C(10)	1.399(3)
O(3)-C(16)	1.377(3)
O(3)-C(13)	1.404(3)
O(4)-C(20)	1.223(3)
O(5)-C(26)	1.377(3)
O(5)-C(29)	1.408(3)
O(6)-C(35)	1.378(3)
O(6)-C(32)	1.401(3)
O(7)-C(39)	1.234(3)
O(8)-C(45)	1.395(3)
O(8)-C(48)	1.398(3)
O(9)-C(54)	1.386(3)
O(9)-C(51)	1.406(3)
C(1)-C(57)	1.487(3)
C(1)-C(4)	1.498(4)
C(2)-C(7)	1.375(5)
C(2)-C(3)	1.380(4)
C(3)-C(4)	1.382(4)
C(4)-C(5)	1.393(4)
C(5)-C(6)	1.386(4)
C(6)-C(7)	1.377(4)
C(8)-C(13)	1.372(4)
C(8)-C(9)	1.384(4)
C(9)-C(10)	1.371(4)
C(10)-C(11)	1.371(4)
C(11)-C(12)	1.383(4)
C(12)-C(13)	1.367(4)
C(14)-C(15)	1.386(4)
C(14)-C(19)	1.387(4)
C(15)-C(16)	1.369(4)
C(16)-C(17)	1.389(4)
C(17)-C(18)	1.379(4)
C(18)-C(19)	1.388(4)
C(19)-C(20)	1.498(4)
C(20)-C(23)	1.489(4)
C(21)-C(26)	1.378(4)
C(21)-C(22)	1.383(4)
C(22)-C(23)	1.390(4)
C(23)-C(24)	1.396(4)
C(24)-C(25)	1.379(4)
C(25)-C(26)	1.384(4)
C(27)-C(28)	1.382(4)
C(27)-C(32)	1.386(4)
C(28)-C(29)	1.381(4)
C(29)-C(30)	1.371(4)
C(30)-C(31)	1.382(4)
C(31)-C(32)	1.375(4)
C(33)-C(34)	1.382(3)

C (33) -C (38)	1.396 (3)
C (34) -C (35)	1.383 (3)
C (35) -C (36)	1.385 (4)
C (36) -C (37)	1.372 (4)
C (37) -C (38)	1.396 (4)
C (38) -C (39)	1.483 (4)
C (39) -C (42)	1.496 (4)
C (40) -C (45)	1.380 (4)
C (40) -C (41)	1.386 (4)
C (41) -C (42)	1.392 (3)
C (42) -C (43)	1.393 (4)
C (43) -C (44)	1.385 (4)
C (44) -C (45)	1.382 (3)
C (46) -C (51)	1.374 (4)
C (46) -C (47)	1.384 (4)
C (47) -C (48)	1.383 (4)
C (48) -C (49)	1.370 (4)
C (49) -C (50)	1.394 (4)
C (50) -C (51)	1.374 (3)
C (52) -C (53)	1.388 (3)
C (52) -C (57)	1.392 (3)
C (53) -C (54)	1.383 (3)
C (54) -C (55)	1.378 (3)
C (55) -C (56)	1.376 (3)
C (56) -C (57)	1.392 (3)
O (61) -C (64)	1.306 (9)
O (61) -C (61)	1.533 (12)
C (61) -C (62)	1.59 (2)
C (62) -C (63)	1.15 (2)
C (62) -C (64)	1.97 (2)
C (63) -C (64)	1.57 (2)
O (65) -C (68)	1.532 (13)
O (65) -C (65)	1.597 (14)
C (65) -C (66)	1.41 (2)
C (66) -C (67)	1.27 (3)
C (67) -C (68)	1.51 (2)

Bond angles (°)

C(7)-O(2)-C(10)	119.6(2)
C(16)-O(3)-C(13)	122.3(2)
C(26)-O(5)-C(29)	119.5(2)
C(35)-O(6)-C(32)	119.1(2)
C(45)-O(8)-C(48)	117.9(2)
C(54)-O(9)-C(51)	116.9(2)
O(1)-C(1)-C(57)	120.4(2)
O(1)-C(1)-C(4)	119.0(2)
C(57)-C(1)-C(4)	120.6(2)
C(7)-C(2)-C(3)	119.3(3)
C(2)-C(3)-C(4)	121.1(3)
C(3)-C(4)-C(5)	118.7(3)
C(3)-C(4)-C(1)	118.6(2)
C(5)-C(4)-C(1)	122.7(2)
C(6)-C(5)-C(4)	120.6(3)
C(7)-C(6)-C(5)	119.1(3)
C(2)-C(7)-C(6)	121.1(3)
C(2)-C(7)-O(2)	115.8(3)
C(6)-C(7)-O(2)	122.9(3)
C(13)-C(8)-C(9)	119.2(3)
C(10)-C(9)-C(8)	119.7(3)
C(9)-C(10)-C(11)	120.7(3)
C(9)-C(10)-O(2)	123.2(3)
C(11)-C(10)-O(2)	115.9(2)
C(10)-C(11)-C(12)	119.8(3)
C(13)-C(12)-C(11)	119.3(3)
C(12)-C(13)-C(8)	121.3(3)
C(12)-C(13)-O(3)	116.7(2)
C(8)-C(13)-O(3)	121.6(2)
C(15)-C(14)-C(19)	120.9(3)
C(16)-C(15)-C(14)	119.6(3)
C(15)-C(16)-O(3)	125.6(2)
C(15)-C(16)-C(17)	120.4(2)
O(3)-C(16)-C(17)	113.9(2)
C(18)-C(17)-C(16)	119.6(3)
C(17)-C(18)-C(19)	120.7(3)
C(14)-C(19)-C(18)	118.6(2)
C(14)-C(19)-C(20)	123.5(3)
C(18)-C(19)-C(20)	117.9(2)
O(4)-C(20)-C(23)	120.8(2)
O(4)-C(20)-C(19)	119.5(3)
C(23)-C(20)-C(19)	119.7(2)
C(26)-C(21)-C(22)	119.0(2)

C(21)-C(22)-C(23)	122.0(2)
C(22)-C(23)-C(24)	117.5(2)
C(22)-C(23)-C(20)	122.9(2)
C(24)-C(23)-C(20)	119.4(2)
C(25)-C(24)-C(23)	121.1(2)
C(24)-C(25)-C(26)	119.7(2)
O(5)-C(26)-C(21)	123.6(2)
O(5)-C(26)-C(25)	115.8(2)
C(21)-C(26)-C(25)	120.6(2)
C(28)-C(27)-C(32)	119.2(3)
C(29)-C(28)-C(27)	119.5(2)
C(30)-C(29)-C(28)	121.2(3)
C(30)-C(29)-O(5)	117.6(3)
C(28)-C(29)-O(5)	121.1(2)
C(29)-C(30)-C(31)	119.4(3)
C(32)-C(31)-C(30)	119.8(2)
C(31)-C(32)-C(27)	120.9(3)
C(31)-C(32)-O(6)	121.7(2)
C(27)-C(32)-O(6)	117.2(3)
C(34)-C(33)-C(38)	121.0(2)
C(35)-C(34)-C(33)	119.5(2)
O(6)-C(35)-C(34)	123.0(2)
O(6)-C(35)-C(36)	116.5(2)
C(34)-C(35)-C(36)	120.4(2)
C(37)-C(36)-C(35)	119.7(2)
C(36)-C(37)-C(38)	121.3(2)
C(33)-C(38)-C(37)	118.0(2)
C(33)-C(38)-C(39)	122.7(2)
C(37)-C(38)-C(39)	119.2(2)
O(7)-C(39)-C(38)	119.3(2)
O(7)-C(39)-C(42)	118.5(2)
C(38)-C(39)-C(42)	122.2(2)
C(45)-C(40)-C(41)	119.0(2)
C(40)-C(41)-C(42)	121.1(2)
C(41)-C(42)-C(43)	118.3(2)
C(41)-C(42)-C(39)	123.2(2)
C(43)-C(42)-C(39)	118.1(2)
C(44)-C(43)-C(42)	121.1(2)
C(43)-C(44)-C(45)	119.1(2)
C(40)-C(45)-C(44)	121.2(2)
C(40)-C(45)-O(8)	122.2(2)
C(44)-C(45)-O(8)	116.5(2)
C(51)-C(46)-C(47)	119.4(2)
C(46)-C(47)-C(48)	119.5(2)
C(49)-C(48)-C(47)	121.1(2)
C(49)-C(48)-O(8)	121.9(2)

C(47)-C(48)-O(8)	116.9(2)
C(48)-C(49)-C(50)	119.3(2)
C(51)-C(50)-C(49)	119.4(2)
C(50)-C(51)-C(46)	121.3(2)
C(50)-C(51)-O(9)	118.5(2)
C(46)-C(51)-O(9)	120.2(2)
C(53)-C(52)-C(57)	121.2(2)
C(54)-C(53)-C(52)	118.6(2)
C(55)-C(54)-C(53)	121.0(2)
C(55)-C(54)-O(9)	115.9(2)
C(53)-C(54)-O(9)	123.1(2)
C(54)-C(55)-C(56)	119.9(2)
C(55)-C(56)-C(57)	120.7(2)
C(56)-C(57)-C(52)	118.5(2)
C(56)-C(57)-C(1)	119.1(2)
C(52)-C(57)-C(1)	122.3(2)
C(64)-O(61)-C(61)	95.3(7)
C(62)-C(61)-O(61)	97.8(10)
C(63)-C(62)-C(61)	76(2)
C(63)-C(62)-C(64)	52.7(12)
C(61)-C(62)-C(64)	71.5(7)
C(62)-C(63)-C(64)	92(2)
O(61)-C(64)-C(63)	98.1(10)
O(61)-C(64)-C(62)	89.3(7)
C(63)-C(64)-C(62)	35.5(7)
C(68)-O(65)-C(65)	106.4(9)
C(66)-C(65)-O(65)	84.9(14)
C(67)-C(66)-C(65)	120(2)
C(66)-C(67)-C(68)	106.2(14)
C(67)-C(68)-O(65)	95.1(13)

Anisotropic Displacement Parameters-U's

Atom	U11	U22	U33	U23	U13	U12
O(1)	49(1)	67(1)	70(1)	-3(1)	-10(1)	13(1)
O(2)	56(1)	90(2)	80(2)	29(1)	17(1)	19(1)
O(3)	94(2)	52(1)	67(1)	-29(1)	-36(1)	17(1)
O(4)	139(2)	53(1)	55(1)	-10(1)	-22(1)	13(1)
O(5)	93(2)	39(1)	51(1)	-14(1)	7(1)	-2(1)
O(6)	81(1)	67(1)	50(1)	-14(1)	-11(1)	-34(1)
O(7)	129(2)	102(2)	55(1)	-38(1)	33(1)	-56(2)
O(8)	45(1)	53(1)	82(1)	-34(1)	-10(1)	1(1)
O(9)	51(1)	40(1)	55(1)	-12(1)	2(1)	-3(1)
C(1)	46(2)	45(1)	52(2)	-12(1)	-8(1)	5(1)
C(2)	43(2)	80(2)	84(2)	11(2)	1(2)	-5(2)
C(3)	44(2)	72(2)	70(2)	-2(2)	-10(1)	2(1)
C(4)	41(1)	53(2)	50(2)	-10(1)	-2(1)	6(1)
C(5)	44(2)	62(2)	56(2)	-6(1)	-4(1)	1(1)
C(6)	50(2)	78(2)	54(2)	1(2)	-5(1)	7(2)
C(7)	47(2)	67(2)	62(2)	6(2)	8(1)	14(1)
C(8)	67(2)	65(2)	49(2)	-18(1)	-1(1)	14(2)
C(9)	68(2)	77(2)	43(2)	0(1)	2(1)	7(2)
C(10)	47(2)	58(2)	59(2)	1(1)	6(1)	7(1)
C(11)	57(2)	65(2)	57(2)	-15(2)	8(1)	4(1)
C(12)	69(2)	58(2)	43(2)	-14(1)	-5(1)	4(1)
C(13)	65(2)	44(1)	50(2)	-18(1)	-14(1)	5(1)
C(14)	78(2)	53(2)	67(2)	-24(2)	-26(2)	4(2)
C(15)	70(2)	53(2)	64(2)	-22(1)	-29(2)	15(1)
C(16)	63(2)	48(2)	42(1)	-18(1)	-8(1)	8(1)
C(17)	68(2)	54(2)	54(2)	-22(1)	-20(1)	8(1)
C(18)	66(2)	55(2)	48(2)	-16(1)	-17(1)	11(1)
C(19)	62(2)	46(2)	45(2)	-14(1)	-7(1)	4(1)
C(20)	75(2)	44(2)	50(2)	-10(1)	-12(1)	5(1)
C(21)	83(2)	38(1)	50(2)	-9(1)	4(1)	-11(1)
C(22)	86(2)	36(1)	55(2)	-12(1)	-3(2)	-7(1)
C(23)	58(2)	40(1)	50(2)	-10(1)	-9(1)	-1(1)
C(24)	55(2)	40(1)	51(2)	-6(1)	-10(1)	0(1)
C(25)	58(2)	34(1)	57(2)	-13(1)	-8(1)	1(1)
C(26)	51(2)	42(1)	48(2)	-15(1)	2(1)	-3(1)
C(27)	55(2)	63(2)	57(2)	-24(1)	-6(1)	-8(1)
C(28)	56(2)	65(2)	57(2)	-26(2)	11(1)	-11(1)
C(29)	65(2)	39(1)	50(2)	-18(1)	5(1)	-8(1)
C(30)	58(2)	44(2)	62(2)	-21(1)	4(1)	-3(1)
C(31)	59(2)	50(2)	55(2)	-21(1)	13(1)	-15(1)
C(32)	61(2)	48(2)	50(2)	-21(1)	-2(1)	-19(1)
C(33)	51(1)	39(1)	45(2)	-17(1)	-11(1)	-2(1)
C(34)	56(2)	41(1)	38(1)	-13(1)	-7(1)	-6(1)
C(35)	50(2)	49(2)	45(2)	-16(1)	-5(1)	-11(1)

C (36)	67 (2)	66 (2)	46 (2)	-25 (1)	-11 (1)	-16 (2)
C (37)	71 (2)	59 (2)	37 (1)	-16 (1)	-3 (1)	-9 (1)
C (38)	50 (1)	42 (1)	41 (1)	-15 (1)	-2 (1)	-2 (1)
C (39)	63 (2)	50 (2)	46 (2)	-16 (1)	6 (1)	-8 (1)
C (40)	49 (2)	42 (1)	50 (2)	-15 (1)	-1 (1)	2 (1)
C (41)	46 (1)	40 (1)	45 (1)	-7 (1)	-1 (1)	-3 (1)
C (42)	53 (2)	37 (1)	40 (1)	-6 (1)	-1 (1)	-1 (1)
C (43)	51 (2)	44 (1)	56 (2)	-16 (1)	8 (1)	-3 (1)
C (44)	42 (1)	49 (2)	64 (2)	-17 (1)	3 (1)	-3 (1)
C (45)	46 (1)	42 (1)	54 (2)	-17 (1)	-6 (1)	1 (1)
C (46)	55 (2)	51 (2)	47 (2)	-24 (1)	-7 (1)	-3 (1)
C (47)	49 (2)	52 (2)	54 (2)	-21 (1)	-12 (1)	-1 (1)
C (48)	39 (1)	41 (1)	54 (2)	-17 (1)	-2 (1)	-4 (1)
C (49)	54 (2)	53 (2)	48 (2)	-25 (1)	-4 (1)	-10 (1)
C (50)	48 (1)	48 (1)	49 (2)	-16 (1)	-9 (1)	-5 (1)
C (51)	43 (1)	37 (1)	46 (1)	-13 (1)	2 (1)	-5 (1)
C (52)	52 (2)	35 (1)	44 (1)	-7 (1)	-6 (1)	0 (1)
C (53)	49 (1)	35 (1)	45 (1)	-10 (1)	-7 (1)	4 (1)
C (54)	46 (1)	42 (1)	35 (1)	-15 (1)	-8 (1)	-5 (1)
C (55)	54 (2)	30 (1)	43 (1)	-11 (1)	-14 (1)	-1 (1)
C (56)	47 (1)	36 (1)	46 (1)	-15 (1)	-15 (1)	6 (1)
C (57)	45 (1)	40 (1)	39 (1)	-12 (1)	-11 (1)	1 (1)
O (61)	300 (9)	510 (15)	177 (6)	-88 (7)	24 (6)	-222 (10)
C (61)	227 (10)	251 (11)	360 (16)	-205 (11)	93 (11)	-60 (9)
C (62)	254 (15)	651 (40)	310 (19)	159 (22)	-129 (13)	-129 (18)
C (63)	381 (21)	300 (15)	451 (25)	61 (15)	-233 (20)	-225 (15)
C (64)	220 (9)	445 (17)	136 (6)	-153 (9)	55 (6)	-152 (11)
O (65)	269 (8)	170 (5)	384 (13)	-70 (7)	-106 (9)	0 (5)
C (65)	229 (11)	390 (20)	275 (14)	-134 (14)	-170 (11)	12 (12)
C (66)	409 (27)	450 (27)	238 (15)	143 (17)	-206 (19)	-142 (21)
C (67)	166 (9)	262 (14)	475 (29)	60 (16)	-18 (12)	-105 (9)
C (68)	377 (21)	282 (15)	222 (13)	-98 (11)	-11 (13)	-43 (14)

C (36)	67 (2)	66 (2)	46 (2)	-25 (1)	-11 (1)	-16 (2)
C (37)	71 (2)	59 (2)	37 (1)	-16 (1)	-3 (1)	-9 (1)
C (38)	50 (1)	42 (1)	41 (1)	-15 (1)	-2 (1)	-2 (1)
C (39)	63 (2)	50 (2)	46 (2)	-16 (1)	6 (1)	-8 (1)
C (40)	49 (2)	42 (1)	50 (2)	-15 (1)	-1 (1)	2 (1)
C (41)	46 (1)	40 (1)	45 (1)	-7 (1)	-1 (1)	-3 (1)
C (42)	53 (2)	37 (1)	40 (1)	-6 (1)	-1 (1)	-1 (1)
C (43)	51 (2)	44 (1)	56 (2)	-16 (1)	8 (1)	-3 (1)
C (44)	42 (1)	49 (2)	64 (2)	-17 (1)	3 (1)	-3 (1)
C (45)	46 (1)	42 (1)	54 (2)	-17 (1)	-6 (1)	1 (1)
C (46)	55 (2)	51 (2)	47 (2)	-24 (1)	-7 (1)	-3 (1)
C (47)	49 (2)	52 (2)	54 (2)	-21 (1)	-12 (1)	-1 (1)
C (48)	39 (1)	41 (1)	54 (2)	-17 (1)	-2 (1)	-4 (1)
C (49)	54 (2)	53 (2)	48 (2)	-25 (1)	-4 (1)	-10 (1)
C (50)	48 (1)	48 (1)	49 (2)	-16 (1)	-9 (1)	-5 (1)
C (51)	43 (1)	37 (1)	46 (1)	-13 (1)	2 (1)	-5 (1)
C (52)	52 (2)	35 (1)	44 (1)	-7 (1)	-6 (1)	0 (1)
C (53)	49 (1)	35 (1)	45 (1)	-10 (1)	-7 (1)	4 (1)
C (54)	46 (1)	42 (1)	35 (1)	-15 (1)	-8 (1)	-5 (1)
C (55)	54 (2)	30 (1)	43 (1)	-11 (1)	-14 (1)	-1 (1)
C (56)	47 (1)	36 (1)	46 (1)	-15 (1)	-15 (1)	6 (1)
C (57)	45 (1)	40 (1)	39 (1)	-12 (1)	-11 (1)	1 (1)
O (61)	300 (9)	510 (15)	177 (6)	-88 (7)	24 (6)	-222 (10)
C (61)	227 (10)	251 (11)	360 (16)	-205 (11)	93 (11)	-60 (9)
C (62)	254 (15)	651 (40)	310 (19)	159 (22)	-129 (13)	-129 (18)
C (63)	381 (21)	300 (15)	451 (25)	61 (15)	-233 (20)	-225 (15)
C (64)	220 (9)	445 (17)	136 (6)	-153 (9)	55 (6)	-152 (11)
O (65)	269 (8)	170 (5)	384 (13)	-70 (7)	-106 (9)	0 (5)
C (65)	229 (11)	390 (20)	275 (14)	-134 (14)	-170 (11)	12 (12)
C (66)	409 (27)	450 (27)	238 (15)	143 (17)	-206 (19)	-142 (21)
C (67)	166 (9)	262 (14)	475 (29)	60 (16)	-18 (12)	-105 (9)
C (68)	377 (21)	282 (15)	222 (13)	-98 (11)	-11 (13)	-43 (14)

Coordinates of hydrogen atoms ($10X^{-3}$)

	x	y	z	U (eq)
H (2A)	16958 (3)	6386 (2)	526 (2)	93
H (3A)	16535 (3)	5322 (2)	1720 (2)	79
H (5A)	12825 (3)	5009 (2)	1163 (2)	69
H (6A)	13296 (3)	6034 (2)	-64 (2)	79
H (8A)	12020 (3)	8789 (2)	-538 (2)	74
H (9A)	13498 (3)	7698 (2)	91 (2)	82
H (11A)	15449 (3)	7552 (2)	-2073 (2)	75
H (12A)	14025 (3)	8672 (2)	-2702 (2)	69
H (14A)	12717 (3)	11610 (2)	-1308 (2)	76
H (15A)	13207 (3)	10230 (2)	-1327 (2)	72
H (17A)	10410 (3)	10513 (2)	-2842 (2)	68
H (18A)	10025 (3)	11912 (2)	-2885 (2)	67
H (21A)	9956 (3)	12276 (2)	639 (2)	71
H (22A)	10423 (3)	11876 (2)	-539 (2)	72
H (24A)	10695 (3)	14284 (2)	-1852 (2)	60
H (25A)	10191 (3)	14691 (2)	-680 (2)	60
H (27A)	11791 (3)	11981 (2)	2697 (2)	68
H (28A)	11832 (3)	12879 (2)	1392 (2)	71
H (30A)	7747 (3)	13502 (2)	1901 (2)	66
H (31A)	7729 (3)	12659 (2)	3222 (2)	66
H (33A)	7120 (3)	9794 (1)	3913 (2)	52
H (34A)	8476 (3)	10924 (2)	3237 (2)	53
H (36A)	9142 (3)	11143 (2)	5370 (2)	68
H (37A)	7808 (3)	10012 (2)	6040 (2)	66
H (40A)	7505 (3)	7231 (2)	3995 (2)	57
H (41A)	7953 (3)	8376 (2)	4388 (2)	54
H (43A)	4184 (3)	8246 (2)	5774 (2)	62
H (44A)	3698 (3)	7132 (2)	5348 (2)	63
H (46A)	7243 (3)	4413 (2)	3372 (2)	59
H (47A)	5627 (3)	5528 (2)	3442 (2)	60
H (49A)	7095 (3)	5725 (2)	5382 (2)	59
H (50A)	8736 (3)	4617 (2)	5300 (2)	57
H (52A)	12146 (3)	5426 (2)	2435 (2)	55
H (53A)	9995 (3)	5208 (1)	3265 (2)	53
H (55A)	11243 (3)	2797 (1)	4201 (1)	49
H (56A)	13412 (3)	3031 (2)	3418 (1)	50
H (61A)	8575 (12)	9764 (7)	-1947 (9)	320
H (61B)	8340 (12)	8897 (7)	-1252 (9)	320
H (62A)	6115 (17)	10253 (15)	-1296 (10)	542
H (62B)	5979 (17)	9512 (15)	-1703 (10)	542
H (63A)	7306 (18)	8758 (10)	-797 (12)	453
H (63B)	5712 (18)	8955 (10)	-435 (12)	453
H (64A)	6542 (11)	10400 (8)	-531 (5)	302
H (64B)	7067 (11)	9662 (8)	196 (5)	302
H (65A)	2002 (12)	8226 (11)	3108 (8)	330
H (65B)	2720 (12)	7660 (11)	3875 (8)	330
H (66A)	4314 (26)	8490 (14)	2822 (10)	468
H (66B)	4727 (26)	7526 (14)	3113 (10)	468
H (67A)	5236 (12)	7717 (9)	1948 (14)	401
H (67B)	4094 (12)	8467 (9)	1730 (14)	401
H (68A)	3727 (18)	6859 (10)	1825 (9)	348
H (68B)	2499 (18)	7585 (10)	1749 (9)	348

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Vita

Mingfei Chen was born in Hefei, China. After getting his BS degree in chemical engineering from Tsinghua University in 1985, he continued his education in polymer science at Tsinghua University and was awarded MS degree in 1988. In his master's thesis, he synthesized first thermotropic polyamide liquid crystals. He was employed as a production engineer for a couple of years by Respiration Inc. in Canton, China. While at Respiration, he helped to establish the plastics injection molding department and supervised about 30 factory workers. He came to the United States in November 1991 to pursue his Ph. D. in chemistry. After brief stay at Virginia Commonwealth University, he transferred to Virginia Tech in 1992 and joined Dr. Gibson's group shortly after. His doctoral dissertation is on macrocyclic monomer synthesis and ring-opening polymerization. His research interests include stereospecific living free radical polymerization, novel nonlinear optical polymeric materials, dendrimeric and hyperbranched conductive polymers, non-isocyanate synthesis of polyurethane and environmentally friendly polymers. Mingfei Chen is a member of American Chemical Society.