Cyclic Aryl Ethers:
New Intermediates for High Performance Polymers

By

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To my colleagues and friends in Montreal

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Abstract

A high yield synthesis of cyclic(aryl ether ketone) oligomers containing a 1, 2-dibenzoylbenzene moiety via the nucleophilic aromatic substitution route has been developed. Chemical transformation of the 1,2-dibenzoylbenzene moiety of these cyclic(aryl ether ketone)s leads to the preparation of novel cyclic(aryl ether phthalazine)s and cyclic(aryl ether isoquinoline)s. Matrix assisted laser desorption ionization - time of flight - mass spectrometry, which enables the detection of oligomers with mass up to 5000 Da, was shown to be a very powerful tool for the analysis and proof of the cyclic nature of the oligomers. A preliminary rheology study on selected cyclic(aryl ether ketone)s shows that the viscosity of the cyclic oligomers is orders of magnitude lower than the high molecular weight polymers. Preliminary study on the melt polymerization of selected cyclic oligomers shows that these materials undergo ring opening polymerization readily in the presence of anionic catalysts such as cesium fluoride to give high molecular weight polymers. Thio-ether containing cyclic(aryl ether)s were discovered to undergo ring opening polymerization at temperatures above 350 °C without the use of catalyst, presumably initiated by a free radical mechanism.

During the study of polymerization of cyclic(aryl ether phthalazine)s, the thermal cross-linking reaction of phthalazine containing poly(aryl ether)s was discovered. Furthermore, through the model compound studies, the first thermal rearrangement reaction of a phthalazine to its structural isomer, a quinazoline was discovered. It was found that heating polyphenylated phthalazines at 360 °C for 30 min gives the corresponding quinazolines in high yield. The less sterically crowded 1,4-bis(4-fluorophenyl)phthalazine gave only a low yield of quinazoline. The finding was confirmed by X-ray crystallographic study.

A facile technique has been developed to end cap the phenolic hydroxy groups present in poly[oxy-1,4-(2,6-dimethylphenylene)](PPO®) resin and its blends with 1,3,2-dioxaphospholanyl chloride. Quantitative derivatization was simply performed in an NMR tube in a short time (1/2 h). The ^{31}P NMR spectra of the derivatized PPO® sample gave well separated signals, allowing the detection and quantification of normal phenolic ends, dibutylaminomethyl phenolic ends, and backbone phenolic groups in the polymer. The assignment of these signals was based on a model compound study. Quantitative determination of phenolic hydroxy groups on three different types of PPO® and its blends was achieved with high precision. Hydroxy content as low as 100 ppm can be detected by our method at this stage.

Des Aryl Éthers: Nouveaux Intermédiaires pour les Polymères de Haute Performance

par Kwok Pong Chan

Sommaire

Des oligomères cycliques contenant les groupements aryl, éther et cétone, écrit généralement cyclique(aryl éther cétone)s, et contenant spécifiquement le groupement dibenzoyl-1,2-benzène ont été synthétisés en haut rendement par une substitution aromatique nucléophile. La transformation chimique du groupement dibenzoyl-1,2-benzène par la réaction de ces cycliques avec l'hydrazine et le benzylamine donne les cyclique(aryl éther phtalazine)s et cyclique(aryl éther isoquinoline)s. La nouvelle technique de spectrométrie de masse, MALDI-TOF (Matrix Assisted Laser Desorption Ionization-Time Of Flight) nous a aidé à détecter les oligomères cycliques avec une masse jusqu' à 5000 Da. Cette technique a démontré d'être un outil puissant pour l'analyse et la confirmation de la structure cyclique. Des études préliminaires de rhéologie sur certains cyclique(aryl éther cétone)s ont démontrés qu'ils ont une viscosité plus basse d'ordres de magnitude de celle correspondante aux polymères de haut poids moléculaire et de même composition. Aussi, des études préliminaires de polymérisation au point de fusion de certains oligomères cycliques ont démontrés que ces matières subissent une coupure du cycle en présence d'un catalyseur anionique comme le fluorure de cesium pour donner des polymères de haut poids moléculaire. Les cyclique(thio ether)s subissent une coupure du cycle à des températures élevées (> 350 °C) sans catalyseur. La polymérisation procède probablement par un mécanisme radicalaire.

Durant les études de polymérisation, on a découvert que les cyclique(aryl ether phtalazine)s forment des polymères avec des liaisons croisées. En plus, des monomères modèles ont démontrés un réarrangement thermique du groupement phtalazine à la molécule isomèrique: le quinazoline. Ainsi en chauffant des derivés de le phtalazine à 360 °C pendant 30 min on obtient les quinazoline correspondants en haut rendement. Le bis(4-fluorophényl)-1,4-phtalazine moins encombré donne un bas rendement de le quinazoline correspondant. La structure de le quinazoline substitué a été confirmé par l'analyse crystallographique à rayon-X.

Une technique facile a été développée pour lier les groupements hydroxyles de phénol présent dans la résine poly[oxy-1,4-(2,6-diméthylphénylene)] (PPO™) avec le 1,3,2-dioxaphospholanyl chloride. On effectue ces liaisons, applicable à tous les phénols, quantitativement en 30 min dans un tube de RMN par mélange des deux composés phénoliques et phosphoriques dans une solution de chloroforme-d et pyridine-d5 3:1. Les

spectra RMN ^{31}P du mélange donne des signaux bien séparés qu'on peut quantifier. D'abord aidé par des phénols modèles on assigne les signaux RMN de ^{31}P à des hydroxyles de dibutylaminomethyl phénol terminant le PPO et ceux dans la chaîne du PPO. Puis par intégration des signaux comparativement à celui d'un phénol standard ajouté on quantifie le groupement hydroxyle dans le PPO. L'analyse quantitative du groupement hydroxyle phénolique de trois différentes résines et mélanges de PPO a été obtenue avec précision. Par cette technique on peut détecter le groupement hydroxyle jusqu'à un minimum de 100 ppm.

Contributions to Original Knowledge

In recent years, the advantages of using cyclic oligomers as precursors of thermoplastics has been well recognized. The cyclic oligomers offer a unique combination of low melt viscosity and the possibility of undergoing controlled polymerization in the melt without the liberation of volatile by-products. However, up to now, no general, convenient and high yield synthesis for cyclic(aryl ether)s has been available. And in most cases, no details of the characterization of these materials were reported. Hence, the studies of their polymerization and physical properties are rather scarce in the literature. Therefore, one of our objectives was to develop a better synthesis and characterization for cyclic(aryl ether) oligomers which have low melt viscosity, and when heated would be transformed by ring opening polymerization into polymers with the required properties without the evolution of any volatile by-products in the process. If successful it would greatly improve the processability of poly(aryl ether)s and broaden their application, especially, in the areas of advanced composites and adhesives.

One of the contributions of this research was the development of a high yield synthesis of cyclic(aryl ether ketone) oligomers containing a 1,2-dibenzoylbenzene moiety via the nucleophilic aromatic substitution route. In addition, chemical transformation of the 1,2-dibenzoylbenzene moiety of these cyclic (aryl ether ketone)s led to the preparation of novel cyclic(aryl ether phthalazine)s and cyclic(aryl ether isoquinoline)s. The cyclic nature of these materials was established and their compositions were fully analyzed by a combination of analytical techniques. A relatively new technique called matrix assisted laser desorption ionization - time of flight - mass spectrometry (MALDI-TOF-MS), which enables the detection of oligomers with mass up to 5000 Da, was shown to be a very powerful tool for the analysis and proof of the cyclic nature of the oligomers.

Preliminary rheology study on selected cyclic(aryl ether ketone)s showed that the viscosity of the cyclic oligomers is orders of magnitude lower than the high molecular weight polymer.

Preliminary study on the melt polymerization of selected cyclic oligomers showed that these materials undergo ring opening polymerization readily in the presence of anionic catalysts such as cesium fluoride to give high molecular weight polymers with good thermal and mechanical properties.

It was discovered that thio-ether containing cyclic(aryl ether)s can undergo ring opening polymerization without the use of catalyst at temperatures above 350 °C, presumably the polymerization is likely initiated through a free radical mechanism. The discovery of the free radical ring opening polymerization of thio-ether containing cyclic(aryl

ether) oligomers provides a new direction in design and polymerization of cyclic(aryl ether) oligomers.

During the study of the polymerization of cyclic(aryl ether phthalazine)s, a thermal cross-linking reaction of phthalazine containing poly(aryl ether)s was discovered. Furthermore, through the model compound studies, the first thermal rearrangement reaction of a phthalazine to its structural isomer, a quinazoline was discovered. It was found that heating polyphenylated phthalazines at 360 ℃ for 30 minutes gave the corresponding quinazolines in high yield. The less sterically crowded 1,4-bis(4-fluorophenyl)phthalazine gave only a low yield of quinazoline. X-ray crystallographic analysis further confirmed our finding.

Utilizing this efficient thermal rearrangement of polyphenylated phthalazines, we have prepared a novel activated difluoride, 2,4-bis(4-fluorophenyl)-5,6,7,8-tetraphenylquinazoline, which underwent high temperature solution polycondensation with 2,2-bis(4-hydroxyphenyl)propane to give a quinazoline containing poly(aryl ether), which is amorphous, has a glass transition temperature of 264 °C and has high thermooxidative stability with 5% weight loss being recorded at 540 °C in nitrogen.

Finally in chapter 4, development of an efficient technique for the determination of microstructures within poly[oxy-1,4-(2,6-dimethylphenylene)] (PPO®)resin based on ^{31}P NMR was presented. The phenolic hydroxy groups present in PPO® resin or its blends were end-capped with 1,3,2-dioxaphospholanyl chloride. This quantitative derivatization was simply done in the NMR tube in a short time (1/2 h). The ^{31}P NMR spectra of the derivatized PPO® sample gave well separated signals allowing the detection and quantification of normal phenolic ends, dibutylaminomethyl phenolic ends, and backbone phenolic groups in the polymer. The assignment of these signals was based on a model compound study. Quantitative analyses of these phenolic groups on three different types of PPO® and PPO® blends was achieved with high precision. Hydroxy contents as low as 100 ppm can be detected by our method at this stage. The development of this technique will greatly enhance the understanding of the processing behavior of PPO®.

List of Publications Originating from Research at McGill University

1 **"Thermal chemistry of poly(aryl ether phthalazine)s and synthesis of poly(aryl ether quinazoline)s."**

K. P. Chan, H. Yang, and A. S. Hay, *Macromolecules*, submitted June 1995.

2 **"Ring-opening polymerization of macrocyclic aryl ether ketone oligomers containing the 1,2-dibenzoylbenzene moiety."**

Y. Wang, K. P. Chan and A. S. Hay, *J. Polym. Sci. Part A: Polym. Chem.*, submitted June 1995.

3 **"Synthesis and novel free-radical ring-opening polymerization of macrocyclic oligomers containing an aromatic sulfide linkage."**

Y. Wang, K. P. Chan, and A. S. Hay, *Macromolecules*, submitted May 1995.

4 **"Rheological and chemorheological studies of cyclic aryl ether ketone and aryl ether thioether ketone oligomers containing the 1,2-dibenzoylbenzene moiety."**

Y. Wang, K. P. Chan and A. S. Hay, *J. Appl. Polym. Sci.*, submitted June 1995.

5 **"Synthesis and characterization of novel cyclic (aryl ether ketone)s, cyclic (aryl ether phthalazine)s and cyclic (aryl ether isoquinoline)."**

K. P. Chan, Y. Wang, X. L. Hronowski, R. J. Cotter, and A. S. Hay, *Macromolecules*, in press.

6 **"Spectroscopic and magnetic resonance elucidation of the structure of the polymer derived from 1,2-dihydro-4-(4-hydroxyphenyl)-1-oxo-(2H)-phthalazine and bis(4-fluorophenyl)sulfone."**

M. Paventi, K. P. Chan, and A. S. Hay, *J. Macromol. Sci.-Pure Appl. Chem.*, in press.

7 **"Thermal rearrangement of a phthalazine to a quinazoline."**

K. P. Chan, and A. S. Hay, *J. Org. Chem.*, 1995, *60*, 3131.

8 **"Convenient synthesis and facile polymerization of cyclic aryl ether ketones containing the 1,2-dibenzoylbenzene moiety."**

K. P. Chan, Y. Wang, and A. S. Hay, *Macromolecules* , **1995**, *28*, 653.

9 **"A facile quantitative analysis of hydroxyl end groups of PPO by ^{31}P NMR spectroscopy."**

K. P. Chan, D. S. Argyropoulos, D. M. White, G. W. Yeager, and A. S. Hay, *Macromolecules* , **1994**, *27*, 6371.

10 **"Polymers from 4-(4-hydroxyphenyl)phthalazin-1-one."**

N. Berard, M. Paventi, K. P. Chan, and A. S. Hay, *Makromol. Chem., Macromol. Symp.*, **1994**, *77*, 379.

Glossary of Abbreviations and Symbols

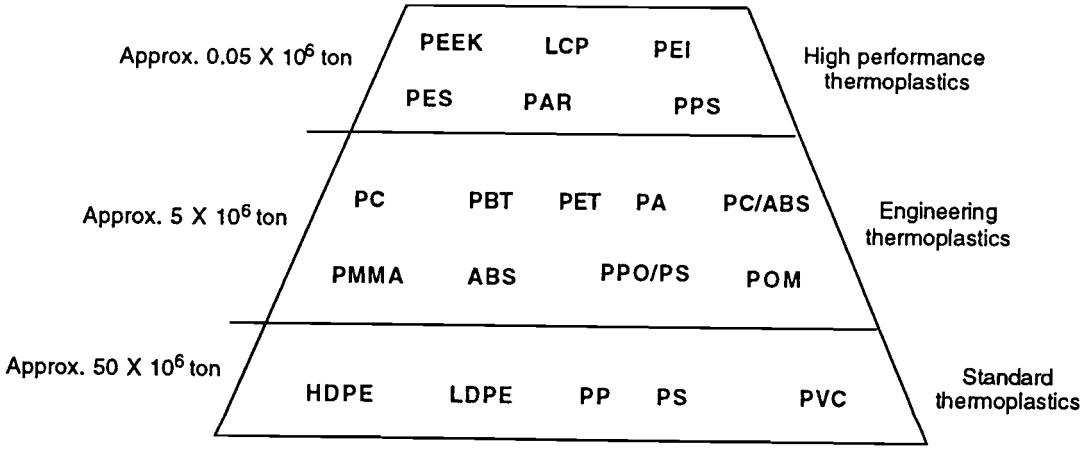
DMAc	N,N-dimethylacetamide
DMF	N,N-dimethylformamide
DMSO	dimethylsulfoxide
DMTA	dynamical mechanical thermal analysis
DSC	differential scanning calorimeter
E'	storage modulus
E''	loss modulus
GPC	gel permeation chromatography
HPLC	high pressure liquid chromatography
MALDI-TOF-MS	matrix assisted laser desorption ionization-time of flight-mass spectrometry
Mn	number average molecular weight
mp	melting point
MS	mass spectrum
Mw	weight average molecular weight
Mw/Mn	polydispersity
NMP	N-methylpyrrolidinone
NMR	nuclear magnetic resonance
ppm	part per million
PPO®	poly[oxy-1,4-(2,6-dimethylphenylene)]
tan δ	ratio of loss modules to storage modulus (E"/E')
Tc	crystallizing temperature
Tg	glass transition temperature
TG/DTA	thermogravimetric / differential thermal analysis
Tm	crystalline melting temperature
	aromatic moieties

Chapter One
Introduction

1.1 Objective

Poly(aryl ether)s are a unique class of polymeric materials. They are characterized by their excellent mechanical strength per unit weight, high thermal stability, and hydrolytic resistance.[1] Therefore, they are referred to as high performance polymers as compared to polyethylene, polystyrene, polymethylmethacrylate, polybutadiene, etc. (Figure 1.1).

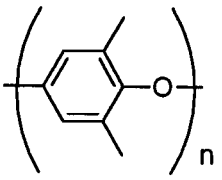
Figure 1.1 Classification of the important thermoplastics and their consumption world wide (1988). [2]

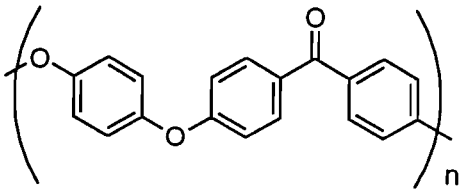


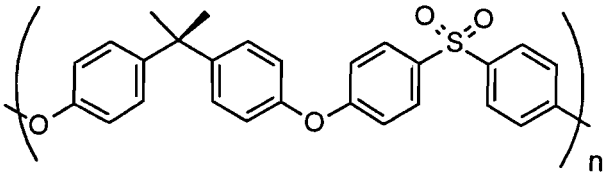
PEEK	Polyetheretherketone	PC/ABS	Polycarbonates / ABS-blend
LCP	Liquid crystalline polyester	POM	Polyoxymethane
PEI	Polyetherimide	PPO / PS	Polyphenyleneoxide / polystyrene-blend
PPS	Polyphenylenesufide	ABS	Acrylonitrile / butadiene / styrene-copolymer
PES	Polyethersulfone	PMMA	Polymethylmethacrylate
PAR	Polyarylate	HDPE	Polyethylene, high density
PC	Polycarbonate	LDPE	Polyethylene, low density
PBT	Polybutylene terephthalate	PP	Polypropylene
PET	Polyethylene terephthalate	PS	Polystyrene
PA	Polyamide	PVC	Polyvinylchloride

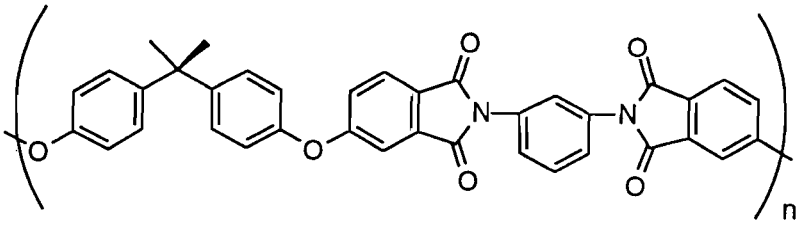
One common feature of this class of polymer is that their structural building blocks are usually a combination of aromatic rings, electron withdrawing groups, and ether linkages. Aromatic rings and electron-withdrawing groups increase the thermal stability and chain stiffness of the resulting polymers, while the ether linkages provide the chain flexibility so that the polymers can have better processability. [3]

Well known examples of commercially available poly(aryl ether)s include poly(phenylene oxide) (PPO®), poly(ether ether ketone) (PEEK®), poly(ether sulfone) (Udel®), and poly(ether imide) (Ultem®).

1.1  **PPO®** Tg = 207 °C

1.2  **PEEK®** Tg = 143 °C, Tm = 343 °C

1.3  **Udel®** Tg = 190 °C

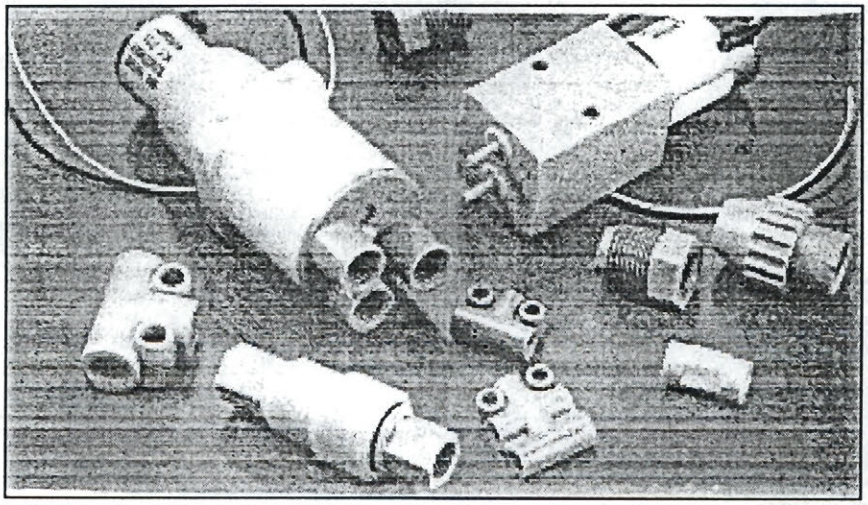
1.4  **Ultem®** Tg = 220 °C

Little known to the general public, poly(aryl ether)s have wide application as structural materials in a number of critical technological areas to replace more conventional materials such as metals and ceramics (Table 1.1 & Figure 1.2).

Table 1.1. Some applications of poly(arylether)s.

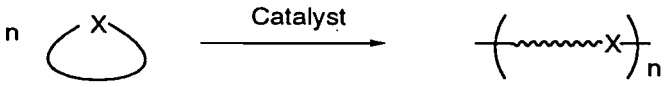
Areas	examples
Microelectronics	circuit broads, insulators
Structural resins for space vehicles	adhesives, composite matrices
Jet engine components	fan blades, flaps
Automotive components	connecting rods, pistons
Fire resistance materials	protective clothing
Medical devices	prostheses

Figure 1.2. ICI's PEEK is used in fluid control components such as these fittings and adapters.



In spite of the excellent properties of poly(aryl ether)s, they are very difficult to process due to their high softening temperature and high melt viscosity. The development of readily processable intermediates of poly(aryl ether)s would undoubtedly broaden the future applications of these excellent materials.[4]

In recent years, the advantages of using cyclic oligomers as precursors of thermoplastics has been well recognized. [5, 6] The cyclic oligomers offer a unique combination of low melt viscosity and the possibility of undergoing controlled polymerization in the melt without the liberation of volatile by-products. We are particularly interested in exploring the opportunity of utilizing cyclic oligomers of poly(aryl ether)s as reactive intermediates. In the area of cyclic(aryl ether)s, pioneering work has been reported by scientists from Imperial Chemical Industries (ICI), General Electric Co. (GE), and Dow Chemical Co..



However, up to now, no general, convenient and high yield synthesis for cyclic(aryl ether)s has been available. And in most cases, no details of the characterization of these materials were reported. Hence, the studies of their polymerization and physical properties are rather scarce in the literature. Therefore, one of our objectives was to develop a better synthesis and characterization for cyclic(aryl ether) oligomers which have low melt viscosity, and when heated would be transformed by ring opening polymerization into polymers with the required properties without the evolution of any volatile by-products in the process. If successful it would greatly improve the processability of poly(aryl ether)s and broaden their application, especially, in the areas of advanced composites and adhesives. There follows a brief survey of the recent developments in the areas of poly(aryl ether)s and cyclic(aryl ether)s syntheses, which can serves as background material, in order to better understand the objectives and strategy of this thesis.

1.2 Survey of poly(aryl ether)s synthesis

The past 50 years witnessed extensive research in the area of poly(aryl ether)s synthesis. Linear high molecular weight poly(aryl ether)s can be prepared by the following synthetic methods, which will be discussed individually.

(1) Electrophilic aromatic substitution.

(2) Ullman ether synthesis.

(3) Oxidative coupling reaction.

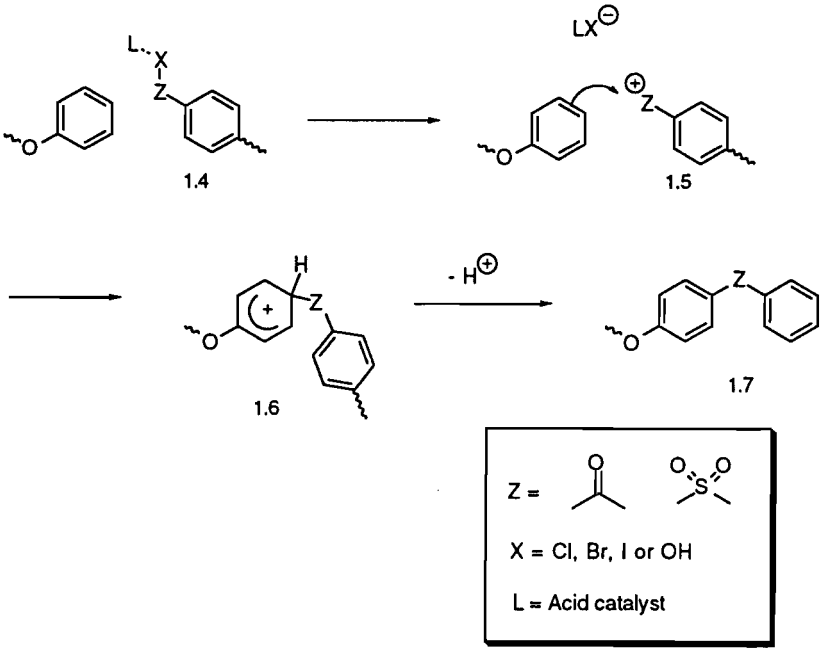
(4) Transition metal catalyzed carbon-carbon coupling reactions.

(5) Nucleophilic aromatic substitution.

Electrophilic aromatic substitution. Electrophilic aromatic substitution reactions such as Friedel Craft acylation and Friedel Craft sulfonylation, are very useful synthetic methods for the synthesis of poly(aryl ether ketone)s and poly(aryl ether sulfone)s respectively. [7,8]

The mechanism of acylation or sulfonylation is shown in Scheme 1.1. The acylium ion or sulfonylium ion **1.5** is formed from the acid halide **1.4** and the catalyst. The attack by **1.5** on an electron rich aromatic nucleus results in the formation of an arenium ion complex **1.6**. This arenium ion loses a proton and the desired sulfonyl or carbonyl linkages **1.7** is formed.

Scheme 1.1

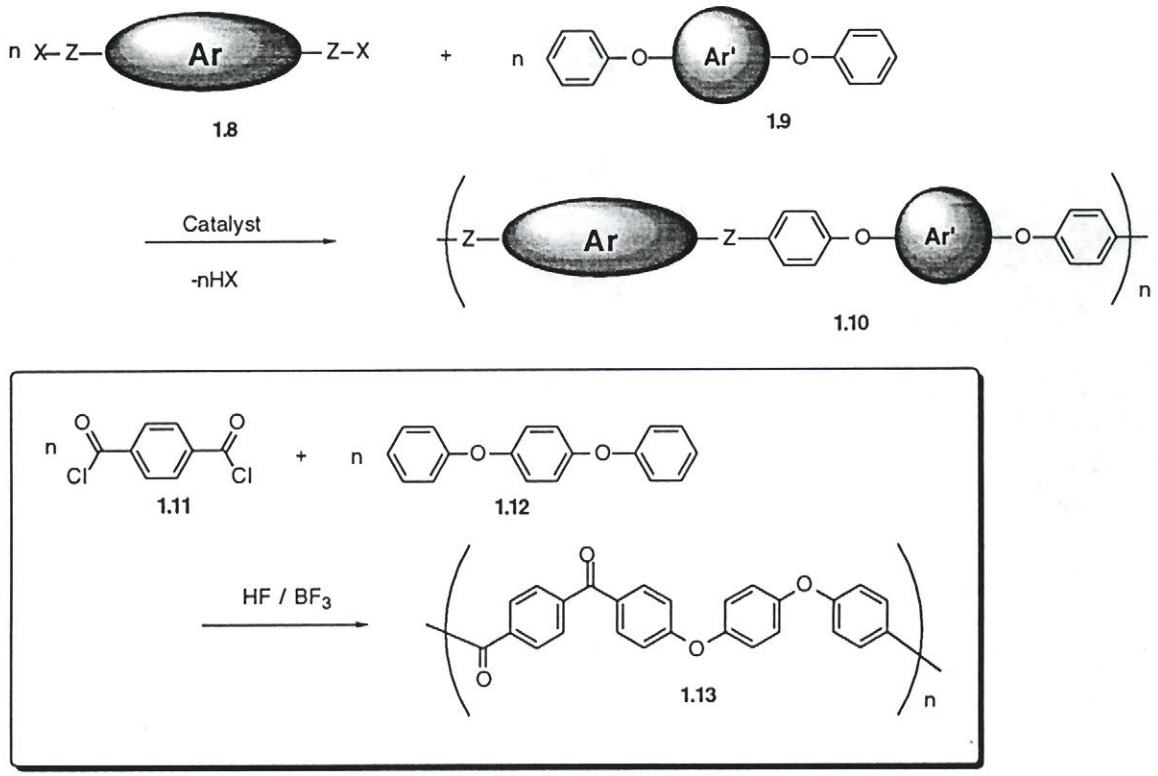


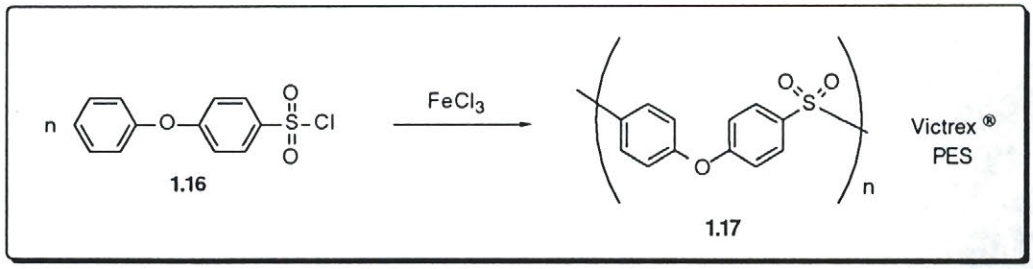
The reaction is of wide scope, and the reagents used are not limited to acyl halides or sulfonyl halides, carboxylic acids or sulfonic acids may also be used. Successful catalyst systems for acid halides include, aluminum trichloride ($AlCl_3$) with lithium chloride (LiCl), boron trifluoride (BF_3), trifluoromethanesulfonic acid (CF_3SO_3H), and iron (III) chloride ($FeCl_3$). When carboxylic or sulfonic acids are used, dehydrating agents such as polyphosphoric acid (PPA), or phosphorus pentoxide (P_2O_5) are used as catalyst.

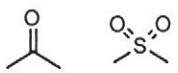
Polycondensation can be carried out between a bis-halide or bis-acid **1.8** and a bis-phenoxy compound **1.9** (Scheme 1.2). For example, the polymerization reaction between terephthaloyl chloride (**1.11**) and 1,4-diphenoxybenzene (**1.12**). Alternatively, monomers that have both halide or acid moiety and the phenoxy moiety **1.14** are also good candidates

for the polycondensation reaction, for example, the preparation of Victrex PES (**1.15**) from 4-phenoxybenzenesulfonyl chloride (**1.17**).

Scheme 1.2



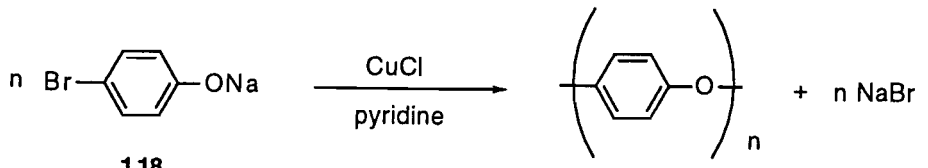


Z =  X = Cl, Br, I or OH L = Acid catalyst

The choice of solvent system is very critical in the synthesis of poly(aryl ether ketone)s. Conventional solvents are ineffective for the preparation of high molecular weight poly(aryl ether ketone)s because these kinds of polymers are usually crystalline or semicrystalline with high melting points (> 350 °C) and not soluble in conventional solvents. However, strong acids such as HF, CF_3SO_3H, or $MeSO_3H$, are good solvents for poly(aryl ether ketone)s. The use of these solvents allows the growing polymer chain to remain soluble during the polymerization, and very high molecular weight materials can be obtained. On the other hand, poly(aryl ether sulfone)s are generally found to be amorphous and can be prepared using conventional solvents such as nitrobenzene.

Ullman ether synthesis. [9] In 1904 Ullman observed that the presence of metallic copper greatly facilitates the substitution of a halogen atom in an aromatic ring by a phenolic anion. This catalytic method for the synthesis of aromatic ethers, is referred as the Ullman ether synthesis. It was later used to prepare poly(phenylene ether) **1.19** from sodium 4-bromophenolate (**1.18**) (Scheme 1.3). [10] The reaction requires an inert atmosphere to avoid the oxidation of the phenol. The optimal temperature is usually 180-220 °C, and pyridine is one of the best solvents. A wide range of copper compounds can be used as catalysts, for example, CuCl, $CuSO_4$, $CuCO_3$, and CuO. The reactivity of the aryl halides is in the order of I > Br > Cl > F. The typical side reaction is reductive dehalogenation.

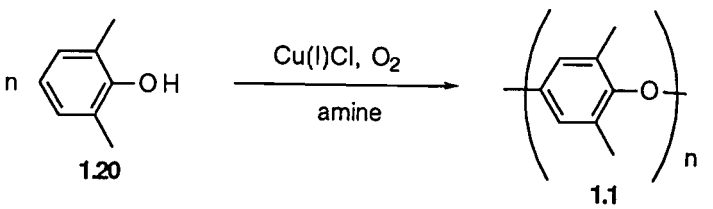
Scheme 1.3



1.18 **1.19**

Oxidative coupling reaction. [11] The synthesis of poly(phenylene ether)s by oxidative coupling of phenols was first reported by Hay et al. in 1959. [12] They reported the synthesis of high molecular weight poly[oxy-(2,6-dimethyl)-1,4-phenylene] (**1.1**) from 2,6-dimethyl phenol (**1.20**) as shown in Scheme 1.4.

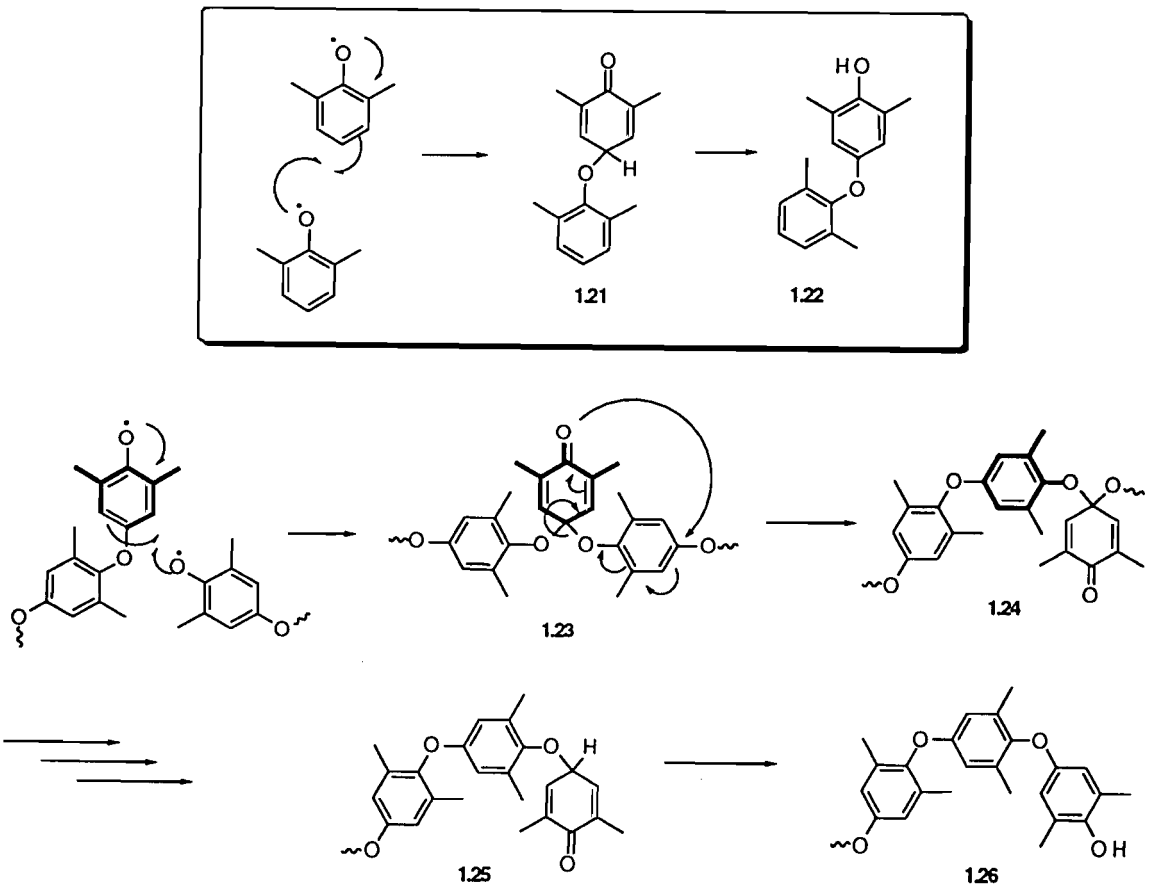
Scheme 1.4



1.20 **1.1**

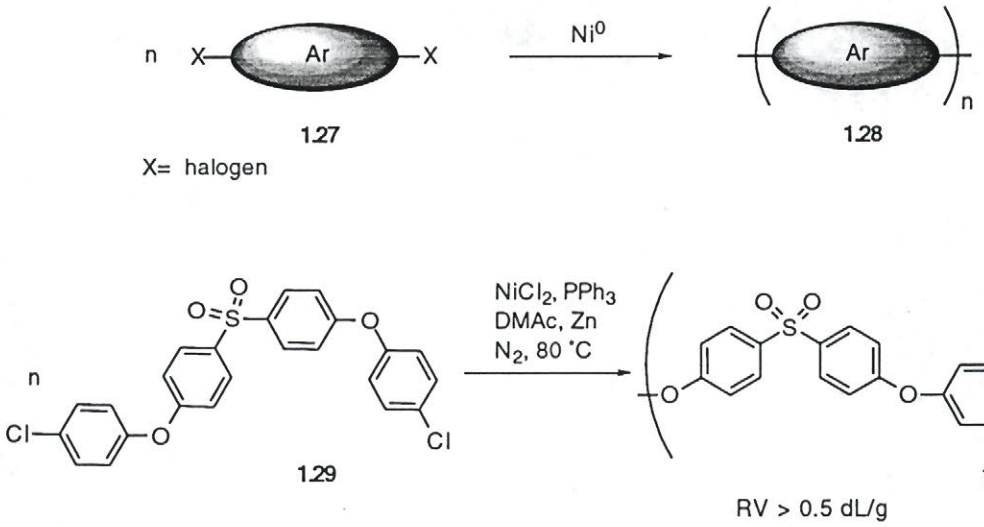
The oxidative coupling polymerization requires a copper(I) complex as catalyst and oxygen as oxidizing agent. A number of 2,6-disubstituted phenols, such as 2,6-diphenylphenol, can be successfully polymerized by this method. One limitation of this polymerization method is the phenolic monomer has to have substituents on the *ortho*-positions so that the polymerization can proceed exclusively through O-C coupling at the *para* -position of the phenol. The key steps in the mechanism of the oxidative coupling polymerization reaction involves coupling of aryloxy radicals to give an unstable quinone ketal **1.23** as shown in Scheme 1.5. It has been suggested that the carbonyl oxygen of a ketal **1.23** is within bonding distance of the *para*-position of the next succeeding ring; thus rearrangement can occur to give a new ketal **1.24** in which the second ring carries the carbonyl oxygen. A sequence of rearrangements can proceed until finally the carbonyl oxygen is located on a terminal ring (**1.25**), and enolization then gives a polymeric phenol **1.26**. This sequence of coupling and rearrangement keep repeating to build up the molecular weight of the polymer as the polymerization reaction proceeds.

Scheme 1.5



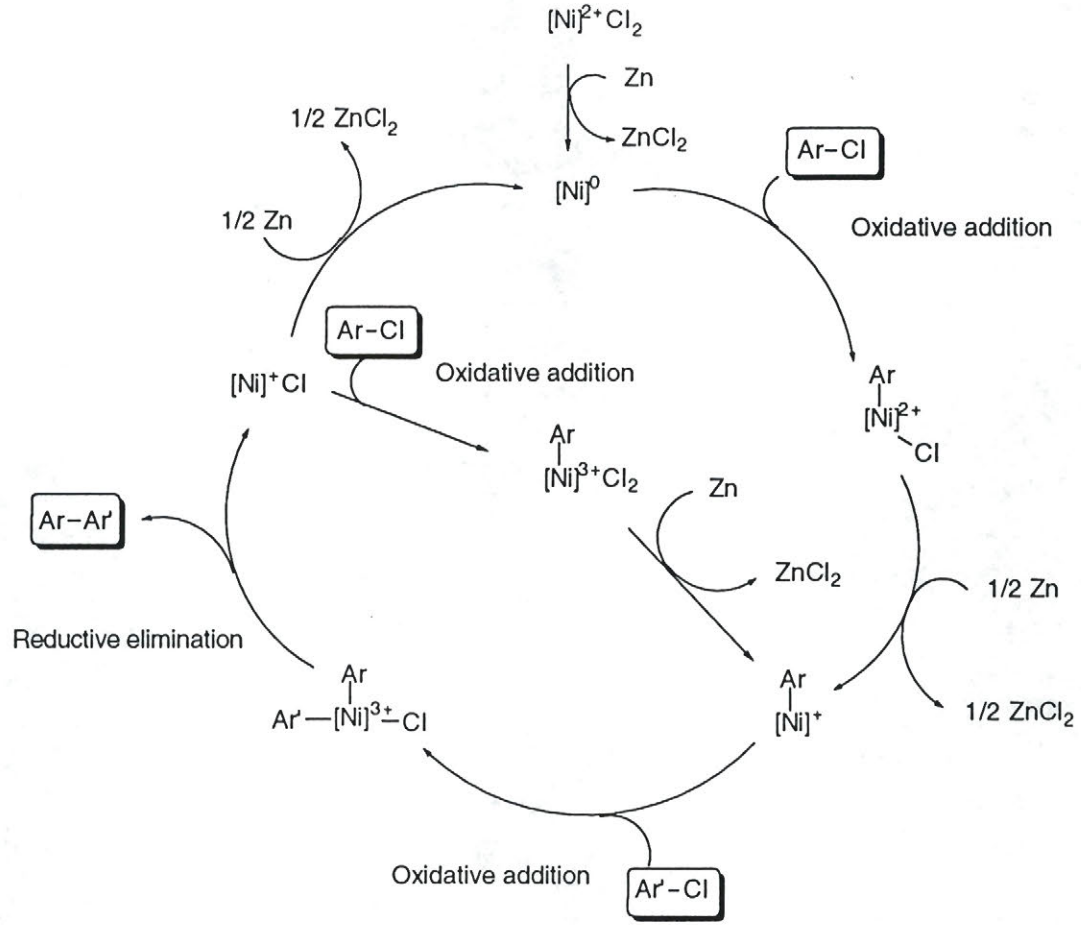
Transition metal catalyzed carbon-carbon coupling reactions. Transition metal catalyzed carbon-carbon (C-C) coupling reactions are attractive methods for the synthesis of aromatic polymers, which are inaccessible by other routes, and have consequently attracted increasing interest in recent years. Heterogeneous systems which employ nickel catalysts and metallic zinc, or magnesium as reducing agents for the polymerization of aromatic dihalides **1.27** have been reported (Scheme 1.6). [13,14] One successful example is the polymerization of 4,4'-bis(*p*-chlorophenoxy)diphenylsulfone (**1.29**) reported by Colon and Kwiatkowski. Polymers with reduced viscosity (RV) higher than 0.5 dL/g can be obtained. The exclusion of water and oxygen, and the use of an excess amount of highly pure zinc are very crucial for obtaining high molecular weight materials.

Scheme 1.6



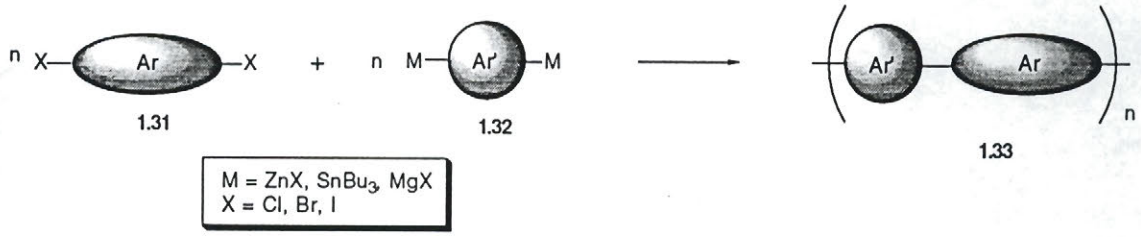
The mechanism of the nickel catalyzed C-C coupling reaction is shown in Scheme 1.7. It is believed to involve the initial oxidative addition of an aryl halide to a nickel(0) to form an nickel(II) intermediate. Subsequent reduction of this nickel (II) intermediate to a nickel (I) species, followed by another oxidative addition of an aryl halide results in a diaryl nickel (III) intermediate. Reductive elimination of this diary nickel (III) intermediate results in the desired C-C bond formation. The active nickel(0) catalyst is continuously regenerated by the zinc employed. Therefore, only catalytic amounts of the nickel compound are required for the reaction. However, the presence of excess amount of zinc is crucial for fast and complete reaction.

Scheme 1.7



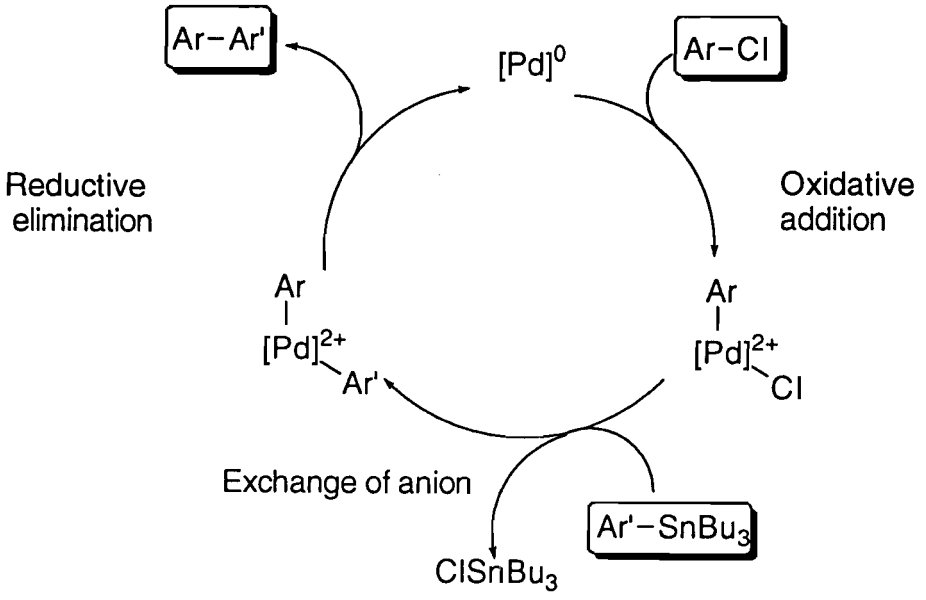
Another successful approach is a palladium catalyzed cross-coupling reaction between an aromatic dihalide **1.31** and difunctional organometallic reagents **1.32**, such as tin, magnesium and zinc (Scheme 1.8). [15,16]

Scheme 1.8



The mechanism of the palladium catalyzed cross coupling reaction between an aryl chloride and an aryl tin reagent is illustrated in Scheme 1.9. The first step involves the oxidative addition of the aryl chloride to a Pd(0) catalyst, followed by exchange of the halide ion with an aryl anion from the aryl tin reagent to give a diaryl Pd(II) intermediate. Subsequent reductive elimination of the diaryl Pd(II) intermediate gives the desired C-C coupling product along with the regeneration of the Pd(0) catalyst.

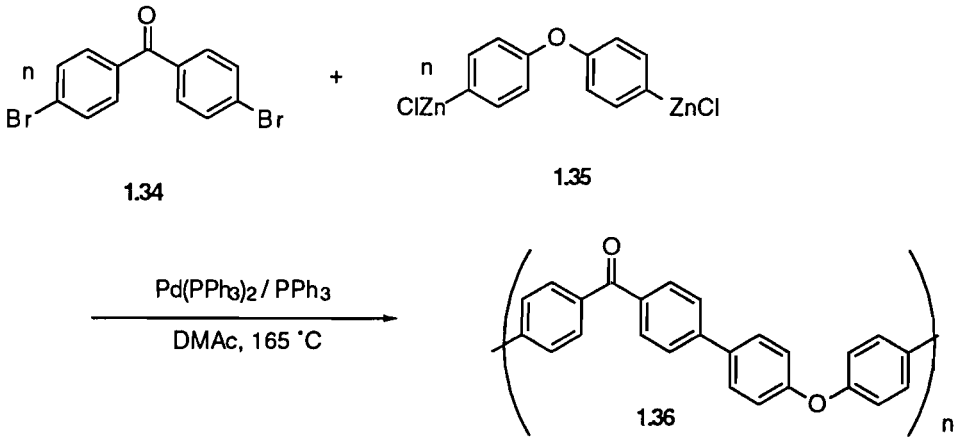
Scheme 1.9



In order to prepare high molecular weight materials by the transition metal catalyzed C-C coupling reactions, an important consideration is that the polymer has to be soluble in the catalyst and solvent system employed; otherwise limited solubility of the growing polymer chain will lead to premature precipitation and termination of chain growth. This is particularly important for the synthesis of poly(aryl ether ketone)s, which are usually crystalline or semicrystalline with high melting points (> 350 °C) and not soluble in conventional solvents as it was mentioned earlier.

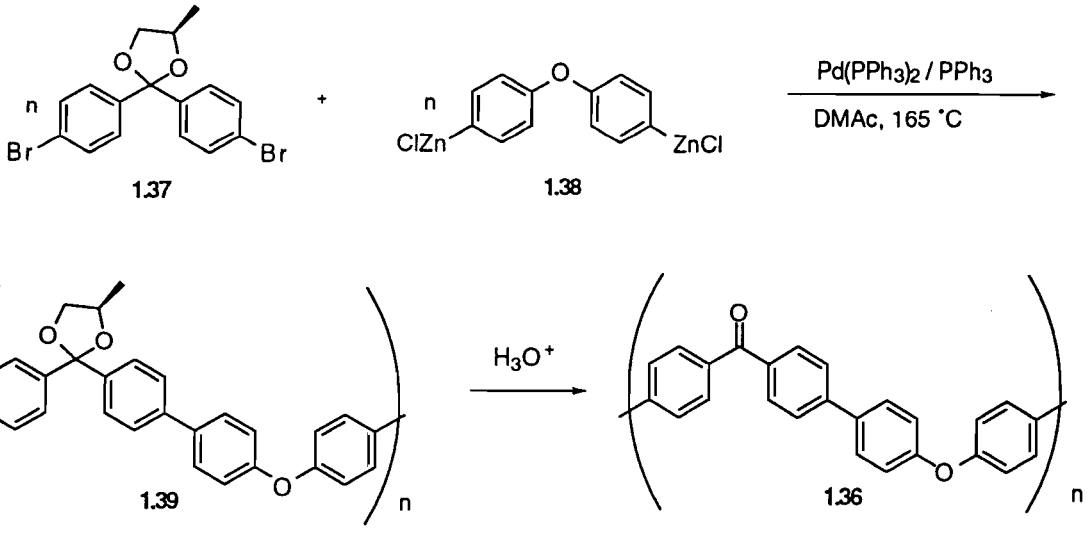
It has been shown that the synthesis of poly(aryl ether ketone) **1.36** from dibromobenzophenone (**1.34**), and bis-chlorozincdiphenylether (**1.35**) by a palladium catalyst failed to yield high molecular weight material (Scheme 1.10a). However, the indirect synthesis of the same poly(aryl ether ketone) **1.36** through a soluble ketal precursor polymer **1.39** proved to be a very successful strategy (Scheme 1.10b).

Scheme 1.10a



Degree of polymerization (DP) = 1.2

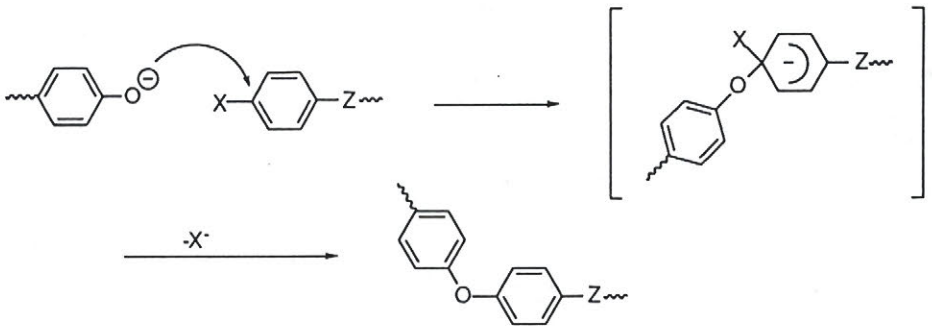
Scheme 1.10b



DP = 19

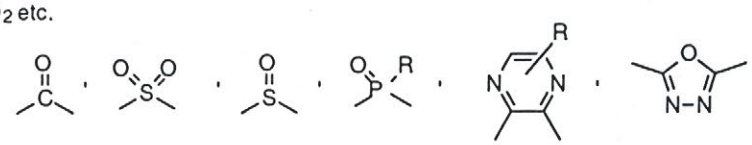
Nucleophilic Aromatic Substitution. The nucleophilic aromatic substitution reaction between activated aromatic halides and phenols as outlined in Scheme 1.11, is one of the most common methods for the synthesis of poly(aryl ether)s. With the appropriate combination of monomers, base and solvent systems, high molecular weight polymers can be conveniently obtained.

Scheme 1.11



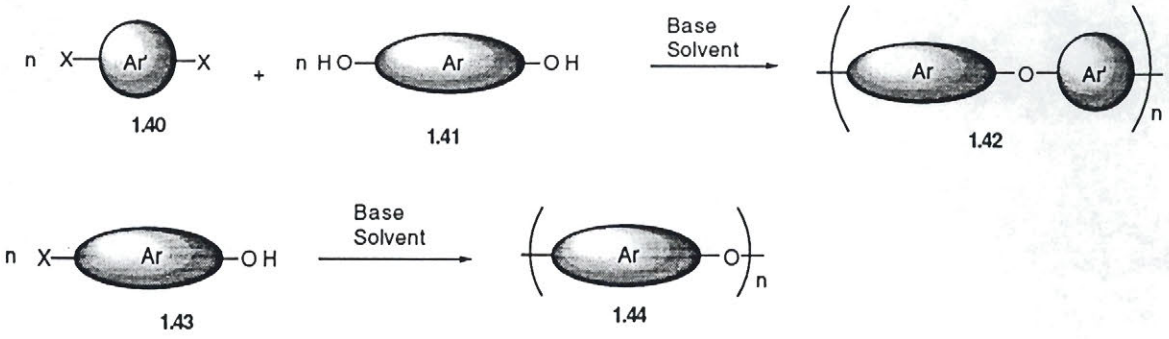
X = leaving group such as F, Cl, Br, NO_2 etc.

Z = elecron withdrawing group, such as



In general, aromatic dihalides **1.40** that are activated by the presence of an electron withdrawing group such as carbonyl, sulfone, sulfoxide, phosphine oxide, or a heterocyclic moiety are reactive enough to be polymerized with bisphenols **1.41**. Alternatively, monomers that have both activated halide moiety and the phenolic moiety **1.43** are also good candidates for the polycondensation (Scheme 1.12). In general the reactivity of aromatic halides is in the order of F >> Cl > Br. A variety of reaction conditions have been developed for this type of polymerization.

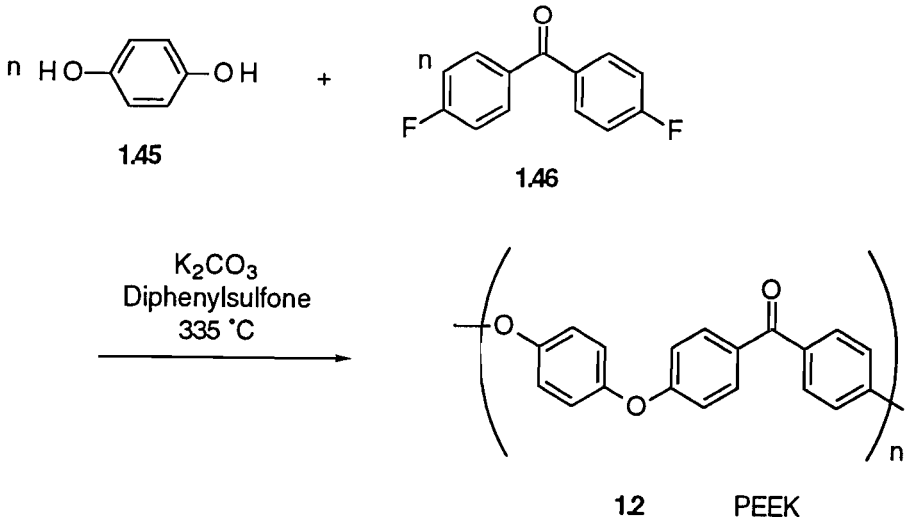
Scheme 1.12



NaOH / DMSO system. [17] The earliest method developed by Johnson et al. employed sodium hydroxide as base, dimethylsufoxide (DMSO) as solvent, and chlorobenzene for azeotropic removal of water from the system. The bisphenol is first treated with stoichiometric amount of sodium hydroxide to give the bisphenol disalt, followed by azeotropic distillation to remove the water. Then the dihalide is introduced into the reaction system which results in the formation of polymer. However, strict observation of stoichiometry between hydroxide and bisphenol is very important for the synthesis of high molecular weight materials, because excess hydroxide will cause a hydrolytic side reaction, in which the hydroxide ion attacks the ether linkage of the polymer and breaks up the growing polymer chain, and reduces the molecular weight of the polymer. Furthermore, it was found that the insolubility and instability of some of the bisphenol disalts precluded successful polymerization.

Carbonate system. [18, 19] A more convenient system using alkali metal carbonates such as sodium or potassium carbonate as base in an polar aprotic solvent has been developed. In the carbonates process, both the bisphenol and the dihalide are introduced at the same time into the reaction vessel containing solvent and carbonate. In contrast to the sodium hydroxide method, the bisphenol disalt is generated in situ by reacting with carbonate during the dehydration process. Smooth formation of high molecular weight polymer is achievable even when using bisphenols whose dialkali metal salt is very insoluble or unstable. Furthermore, hydrolytic side reactions were not found in the presence of excess amount of carbonate. One excellent example is the commercial production of PEEK by ICI using this carbonate process as shown in Scheme 1.13 which cannot be obtained using the sodium hydroxide process. [20]

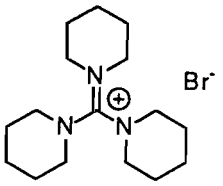
Scheme 1.13



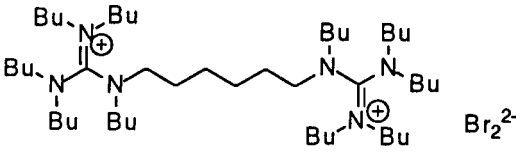
1.45 1.46

1.2 PEEK

Use of Phase Transfer Catalysts (PTC). Brunelle has reported synthesis of high molecular weight poly(aryl ether)s using a PTC catalyzed nucleophilic aromatic substitution polymerization reaction between bisphenol disalts and activated aromatic dihalides. [21] One advantage of this reported method is the use of a less expensive non-polar solvent instead of polar aprotic solvents for the nucleophilic aromatic substitution polymerization. Polar aprotic solvents, such as DMSO or N,N-dimethylacetamide (DMAc) are expensive, difficult to purify and difficult to keep dry, since they readily dissolve water. Thus, the ability to replace polar aprotic solvents with non polar solvents such as 1,2,4-trichlorobenzene, 1,2-dichlorobenzene could make the process more commercially viable. For example, high molecular weight poly(ether imide) **1.4** can be synthesized from disodium salt **1.49**, and dichloro-monomer **1.50** using *o*-dichlorobenzene as solvent and a catalytic amount of the PTC **1.47** (Scheme 1.14).

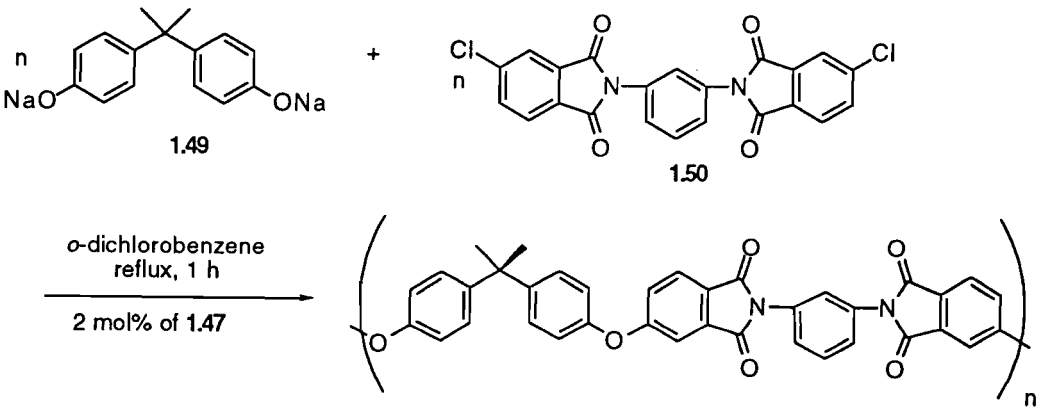


1.47



1.48

Scheme 1.14



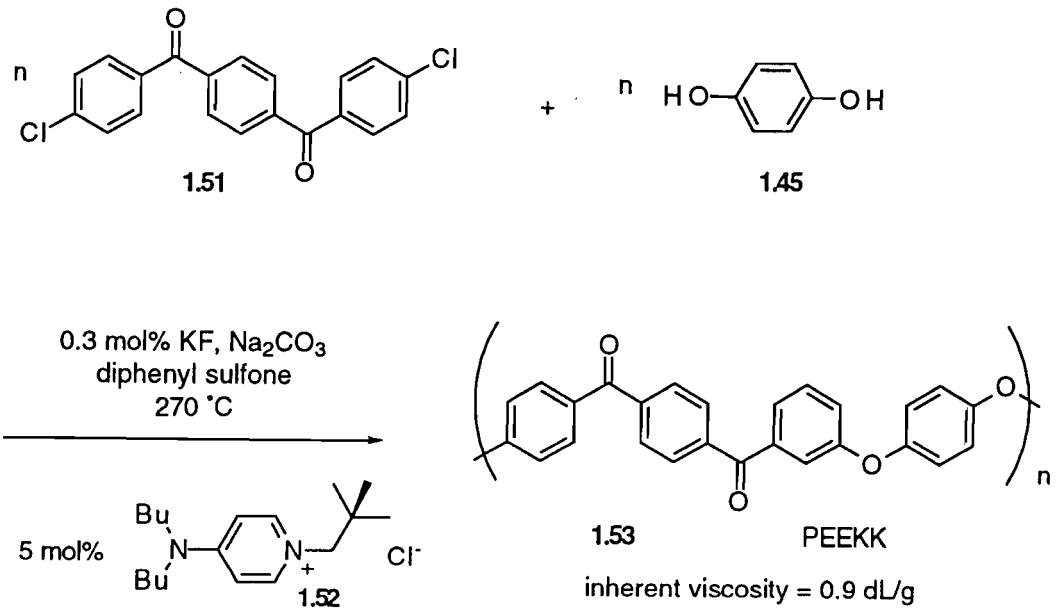
M_w = 64,000 g/mol **1.4**

The key to the success of the Brunelle method is his design of novel thermally stable phase transfer catalysts. The kind of phase transfer catalysts used are hexaalkylguanidinium salts, i.e. tris(piperidino)guanidinium bromide (**1.47**) and α,ω-bis(pentaalkylguanidium)alkane salts, i.e. 1,6-bis(N,N',N',N'',N''-penta-n-butyl-guanidinium)hexane dibromide (**1.48**). Conventional phase transfer catalysts, such as

tetramethylammonium bromide, are unstable at high temperature in the presence of base. Hoffmann elimination or alkylation of the base are commonly observed decomposition processes.

Recently, Mullen et al. reported the use of a thermally stable PTC **1.52** to improve the synthesis of a semicrystalline poly(aryl ether ketone) **1.53**, commercially known as PEEKK, from dichloro-monomer **1.51** and hydroquinone **1.45** via nucleophilic aromatic displacement. High molecular weight material was obtained (Scheme 1.15). [22] They believed that the PTC increased the rate of polymerization by solubilizing the poorly soluble phenolates. Uncatalyzed polymerization only gives low molecular weight materials (inherent viscosity = 0.3 dL/g).

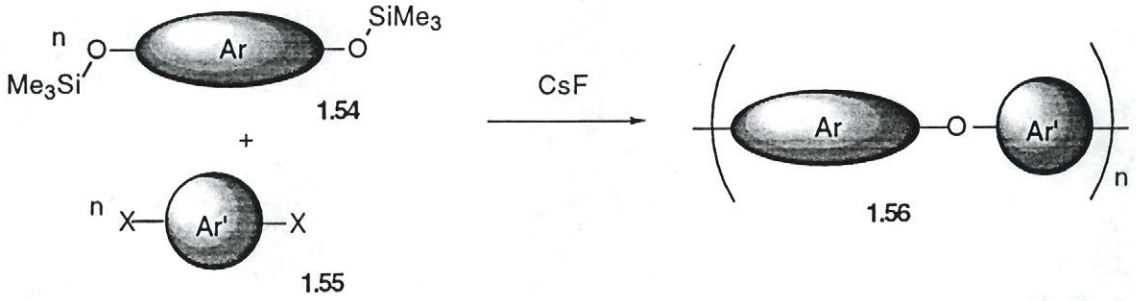
Scheme 1.15



In general, synthesis of high molecular weight semicrystalline poly(aryl ether ketone)s such as **1.53** required the use of very reactive difluoro-monomers. The use of cheaper dichloro-monomers is not feasible due to their low reactivity. Furthermore, dichloro-monomers were found to undergo reductive dechlorination side reactions, which led to premature termination of the polymerization. [23]

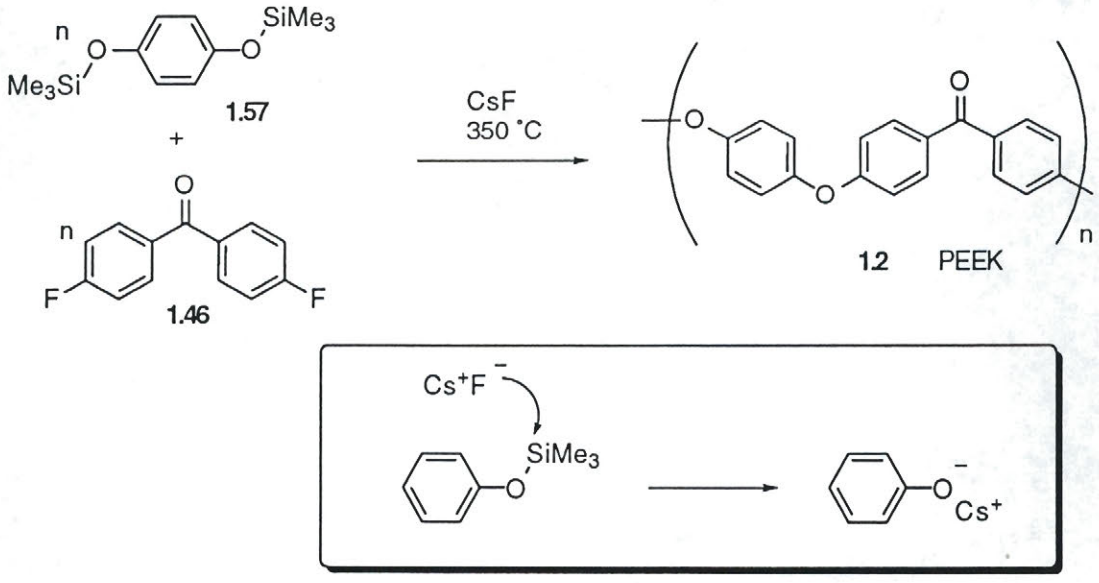
Silylated bisphenols. Kricheldorf et al. reported the use of disilylated bisphenols **1.54** for the preparation of poly(aryl ether)s in the melt using CsF as catalyst (Scheme 1.16a).[24]

Scheme 1.16a



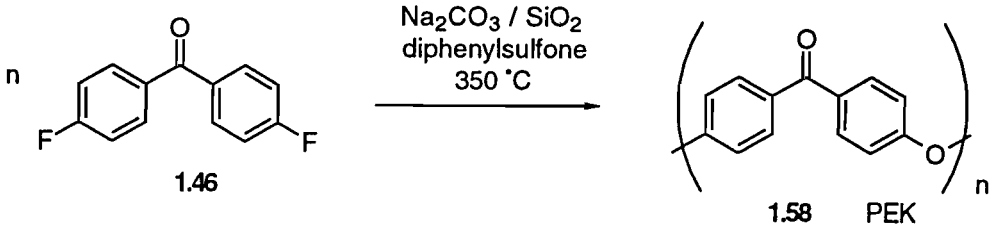
For example, polymerization of silylated hydroquinone (**1.57**) and difluorobenzophone (**1.46**) was catalyzed by CsF and afforded high molecular weight PEEK (Scheme 1.16b) The fluoride anion cleaves the Si-O bond on the silylated hydroquinone (**1.57**) and generates the phenoxide ion which reacts with the difluoro-compound **1.46**. The advantages of this polymerization method are that the polymers can be obtained in a highly pure form without the need of separation from solvent and by-product salts. It has been found that block copolymers of poly(aryl ether)s can also be prepared by this method, as ether interchange reaction that are found in conventional carbonate or sodium hydroxide processes are precluded. [25]

Scheme 1.16b



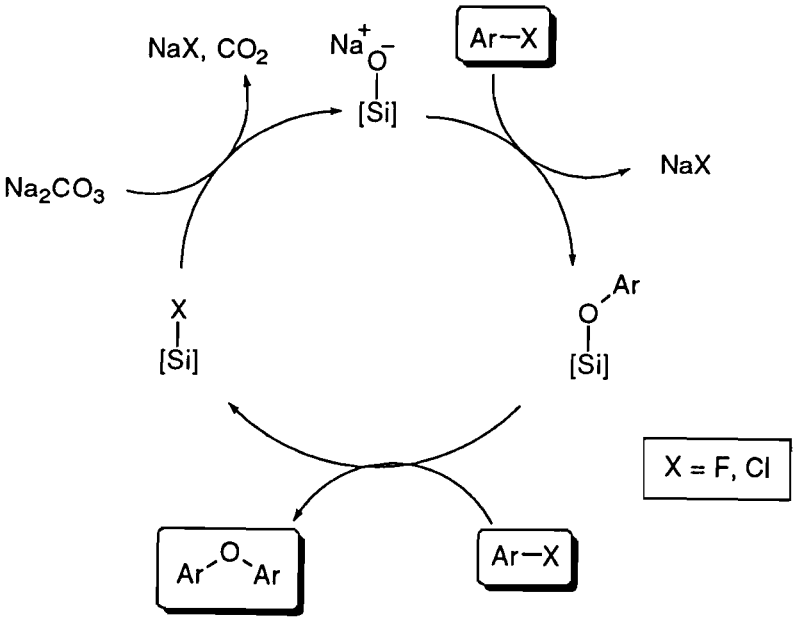
Etherification of aromatic dihalides by alkali metal carbonates. Fukawa et al. reported a very interesting method for the synthesis of poly(aryl ether)s from activated aromatic dihalides using a alkali metal carbonate base and silica as catalyst Bisphenols are not required. [26, 27] For example, high molecular weight poly(ether ketone) (PEK) can be obtained from polyetherification of difluorobenzophenone (**1.46**) as shown in Scheme 1.17.

Scheme 1.17



The etherification reaction is believed to proceed through the following steps as shown in Scheme 1.18. First, free hydroxy groups on the surface of silica are deprotonated by carbonate to give a reactive silyloxide intermediate. A substitution reaction between the reactive silyloxide intermediate and an aromatic halide gives a silylarylether, which undergoes another condensation with an aromatic halide to yield the desired diaryl ether. Aromatic fluorides activated by an electron withdrawing group are most reactive. In the case of less reactive aromatic chlorides, a catalytic amount of a copper salt, such as CuCl, is required to promote the reaction.

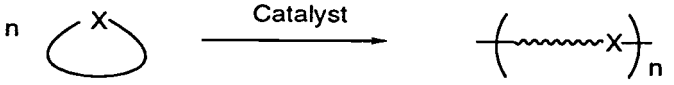
Scheme 1.18



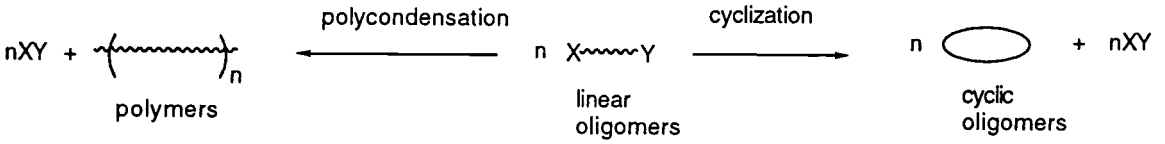
1.3 Survey of cyclic(aryl ether) oligomers synthesis and polymerization

Cyclic oligomers have long been found to be present in low concentration in polymers prepared by condensation polymerization. [28] For example, cyclic oligomers of poly(phenylene sulphide) (PPS) [29], poly(ether ether ketone) (PEEK) [30], and polycarbonate of bisphenol-A (BPA) [31], have been isolated from their parent polymers by solvent extraction and characterized.

Recently, there has been considerable interest in industry to make use of these cyclic oligomers as reactive intermediates for the synthesis of high molecular thermoplastics. The cyclic oligomers offer an unique combination of low melt viscosity and the possibility of undergoing controlled polymerization in the melt without the liberation of volatile byproducts.



The synthesis of cyclic oligomers is not trivial especially if one would like to prepare these materials conveniently in high purity and high yield. Synthesis of cyclic oligomers is very often complicated by the formation of linear oligomers and high molecular weight polymer via competing polycondensation reaction.



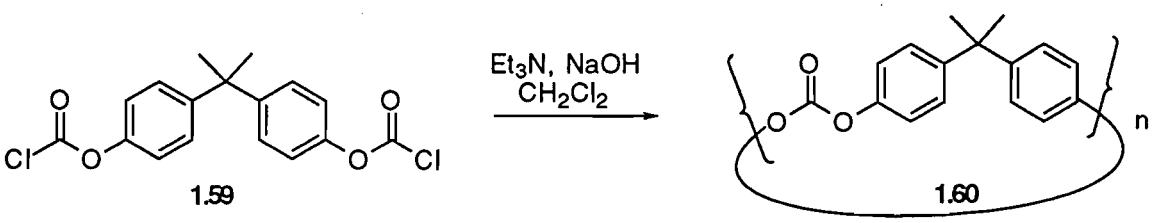
X, and Y complimentary functional groups for coupling reactions.

Selective formation of cyclic oligomers can be achieved by the use of dilute conditions which favor cyclization and suppress polycondensation, since cyclization is a first order reaction and polycondensation is a second order reaction. However, using a large volume of solvent would not be a viable approach. In order to achieve a practical synthesis of cyclic oligomers, a pseudo-high dilution principle [32] was used to achieve high yields of cyclic oligomers. Instead of using a large amount of solvent, a pseudo-high dilution condition can be created by slow addition of the reactants into the reaction vessel at such a rate that a steady low concentration of unreacted end-groups is maintained and, hence, favoring the formation of cyclic oligomers even with a very high product concentration build up. One critical factor in applying the high dilution principle is the

choice of the rate of addition of reactants, which is very much dependent on the rate of reaction.

The first example which demonstrated that cyclic oligomers can be conveniently prepared in high purity and high yield was reported by Brunelle et al. of the GE Co. with the synthesis and polymerization of cyclic carbonates.[33] He reported that slow addition of a solution of BPA-bischloroformate (**1.59**) to an efficiently stirred mixture of methylene chloride, triethylamine, and aqueous sodium hydroxide effected a remarkable selective formation of cyclic oligomeric BPA carbonates (**1.60**) (Scheme 1.19). The product was composed solely of a mixture of cyclic oligomers from dimer to dodecamer. The level of linear oligomers present was estimated to be 0.01 - 0.03 %. The selectivity of cyclic versus linear oligomers achieved was about 10,000 to 1. Furthermore, it was demonstrated that polymerization of the cyclic oligomers occurred in the melt at 200 °C to 300 °C with various catalysts.

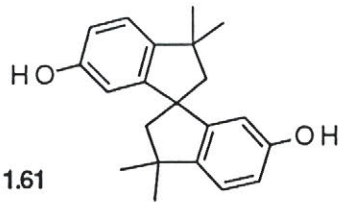
Scheme 1.19



1.59 1.60

Cyclic(aryl ether)s. In the area of cyclic(aryl ether)s, Cella et al. of the GE Co. were first to report synthesis of a series of cyclic(ether ketone)s, cyclic(ether sulfone)s, and cyclic(ether imide)s in the form of an oligomeric mixture in moderate to good yield in 1989 (Schemes 1.20, 1.21 &1.22). [34] The cyclic(ether ketone)s and cyclic(ether sulfone)s oligomers were prepared by a nucleophilic aromatic substitution reaction using the conventional carbonate process without the use of a pseudo-high dilution condition, and reactant concentrations as high as 67 mM were used (Scheme 1.20). The cyclic(ether imide)s oligomers were prepared by an imidization reaction between dianhydrides and diamines by slow delivery of reactants over a period of one hour followed by an additonal reaction time of 2 hours with the final reactants concentration only 17 mM (Schemes 1.21 &1.22). The key to their synthesis is the use of spirobiindane containing monomers **1.61**, **1.64 & 1.67**. The structural rigidity and orthogonal orientating configuration of the spirobiindane group promotes cyclization, and hence, led to good yield of the cyclic oligomers.

Scheme 1.20



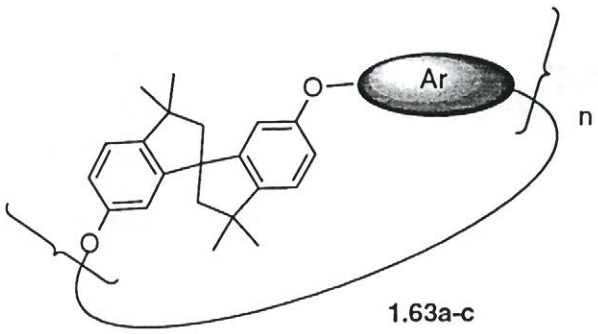
1.61

+

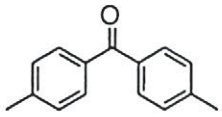
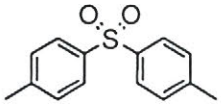
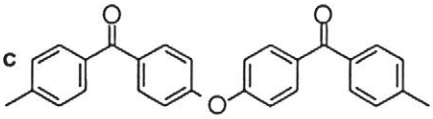
1.62a-c

conc.= 66.7 mM

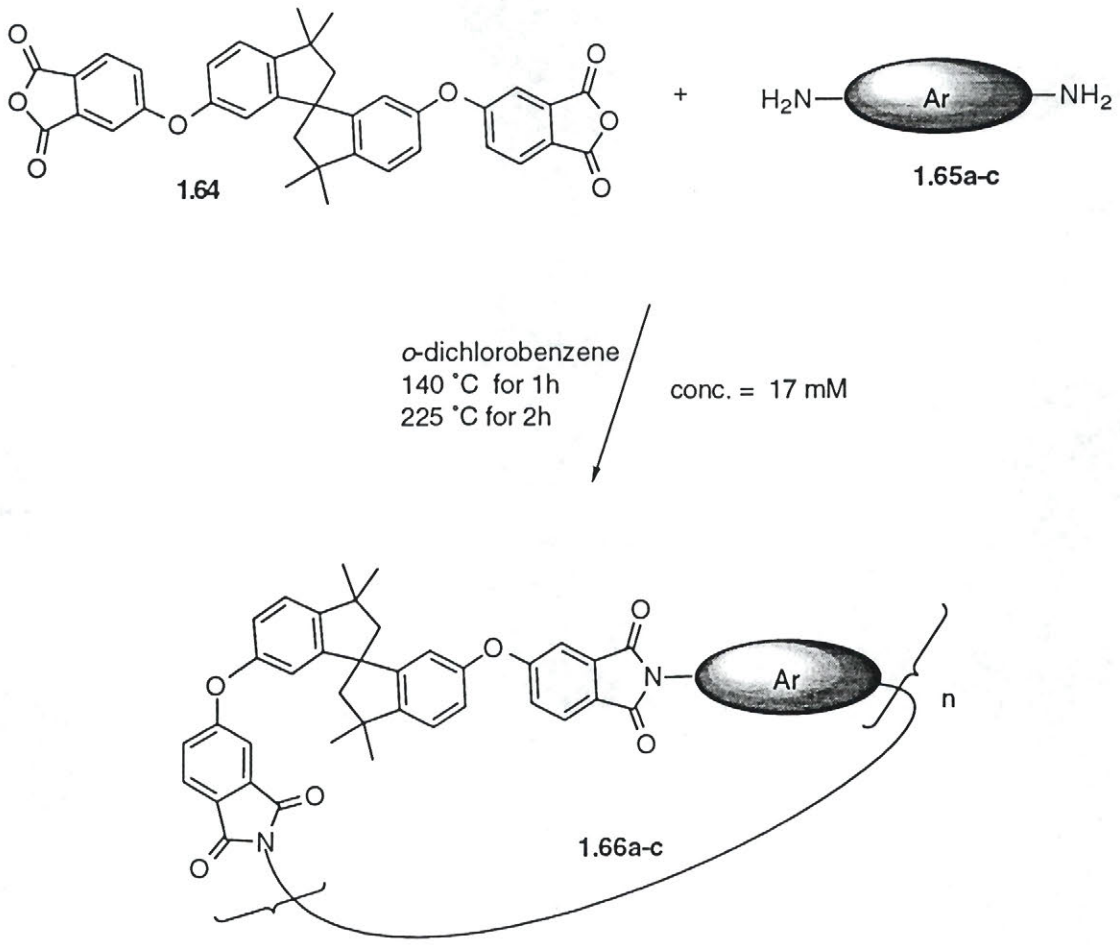
DMSO /Toluene
K_2CO_3
140 -150 °C
4 h



1.63a-c

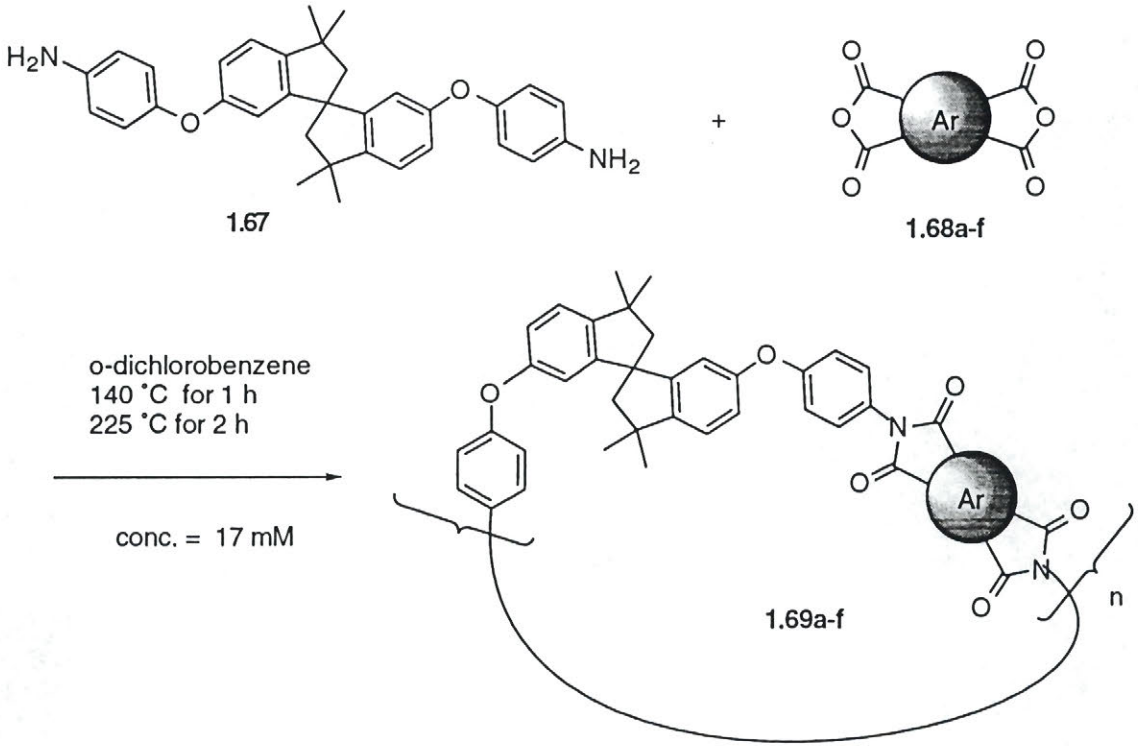
Ar	Yield (%)
a 	47
b 	90
c 	40

Scheme 1.21



Ar	yield (%)
a	77
b	50
c	25

Scheme 1.22



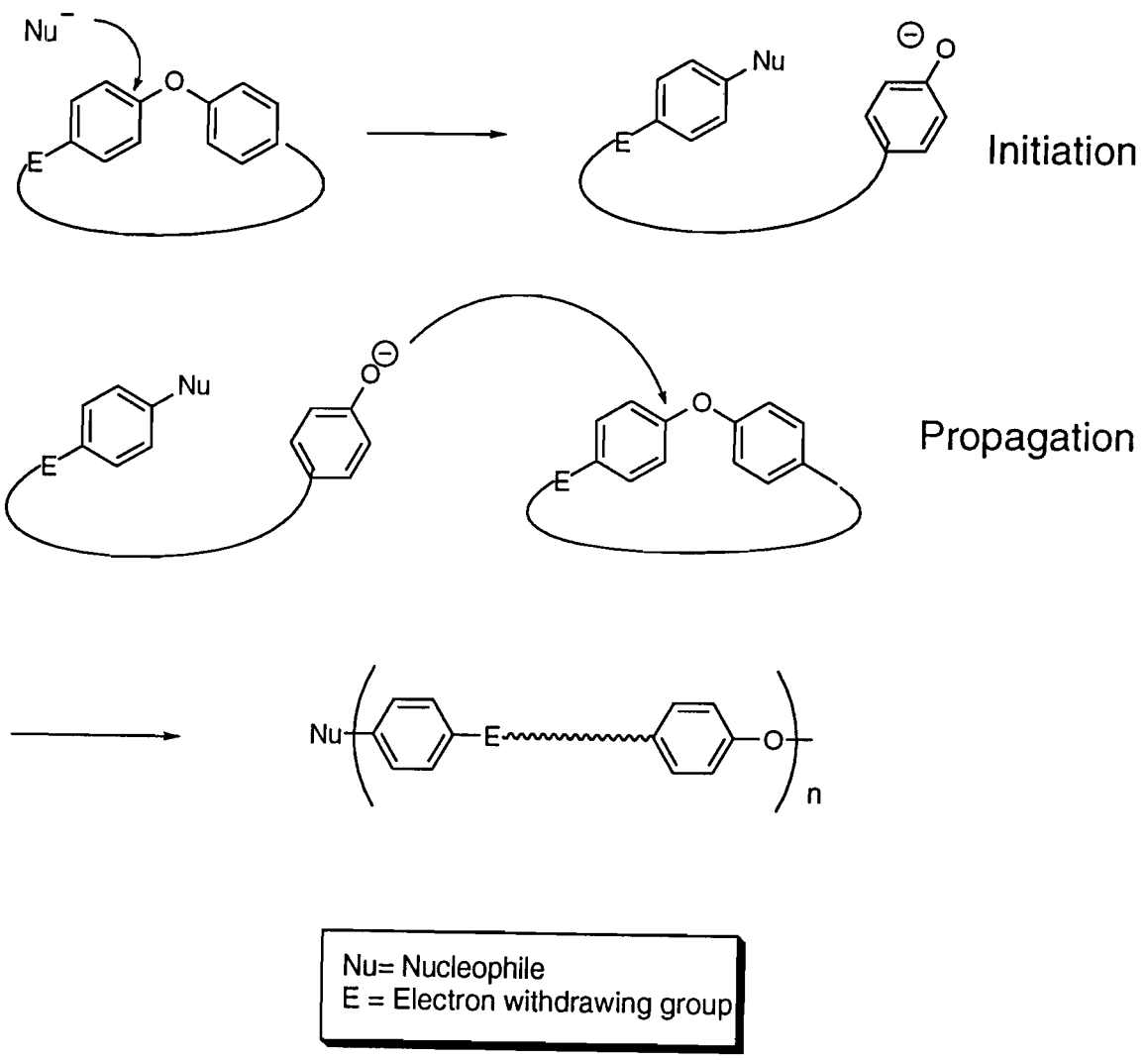
	yield (%)
a	30
b	40
c	75

	yield (%)
d	40
e	45
f	40

They found that these cyclic(ether ketone), cyclic(ether sulfone), and cyclic(ether imide) oligomers suffer from same disadvantage being high melting, crystalline solids which are only sparingly soluble in common organic solvents. Accordingly, they do not lend themselves readily to solution or melt polymerization. In the systems in which melt polymerizations are possible, low molecular weight oligomers were found in the polymerized materials. For example, melt polymerization of cyclic(ether sulfone) **1.63b** required a high conc. of 2,2-bis(4-hydroxyphenyl)propane disodium salt (10 mol %) as catalyst at a very high temperature (380 - 400 °C), and the resulting polymer had a weight average molecular weight (M_w) about 80,000 g/mol. [35]

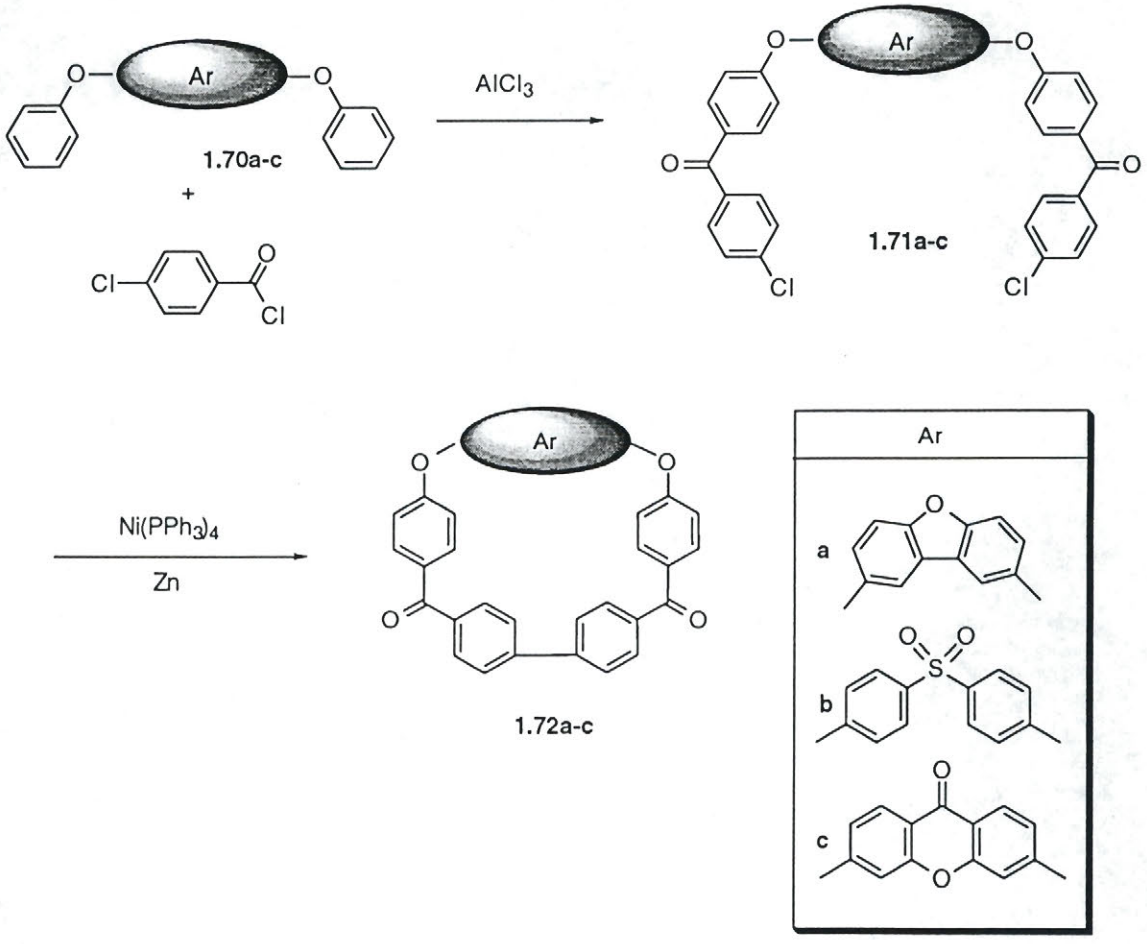
The ring opening polymerization is presumably initiated through an ether exchange reaction. An aryl ether linkage that is activated by an electron withdrawing group has been found to undergo ether exchange reaction readily (Scheme 1.23).[36]

Scheme 1.23



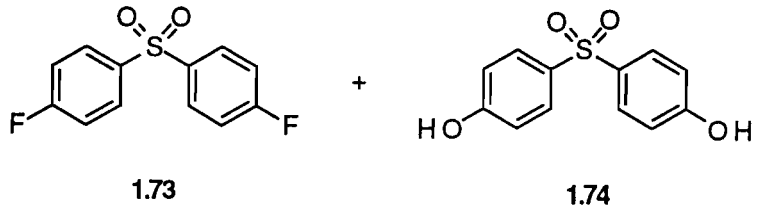
In 1990, Colquhoun et al. of ICI reported the synthesis of cyclic(aryl ether ketone)s by a nickel(0) catalyzed C-C coupling reaction (Scheme 1.24). [37] Instead of obtaining a mixture of cyclic oligomers, they prepared single sized cyclic monomers in 40% yield under pseudo-high dilution conditions. However, no details of the conditions of the reaction were reported for comparison. Polymerization of the cyclic monomer **1.72a** by catalytic amount (1-5 mol%) of cesium fluoride or potassium salt of 4-hydroxybenzophenone at the melting point of the cyclic monomer **1.72a** (353 °C) was found to be highly exothermic. This is consistent with the X-ray crystal structure of **1.72a**, which indicates that the cyclic monomer is highly strained. The polymerization was completed in 2-5 min. The resulting polymer is partially soluble in sulfuric acid, which indicated a slight degree of cross-linking. Fully soluble polymer (inherent viscosity = 0.4 - 0.7 dL/g) was obtained when 1-2 mol% of end-capping reagent was used.

Scheme 1.24



In 1991, Mullins et al. of the Dow Chemical Co. reported the synthesis of cyclic(ether sulfone) **1.75** from 4,4'-difluorodiphenylsulfone (**1.73**) and 4,4'-dihydroxy-diphenylsulfone (**1.74**) in 39% yield (Scheme 1.25). [38] They also reported an alternative method for the synthesis of cyclic(ether sulfone) **1.75** from 4-fluoro-4'-hydroxyldiphenylsulfone (**1.76**) (Scheme 1.25). The yield of cyclic oligomer was 40% with a number average molecular weight (M_n) = 1,800 g/mol. [5] Based on rheometry studies, it was found that the melt viscosity of the cyclic(ether sulfone) **1.75** was 1000 times lower than the linear poly(ether sulfone).

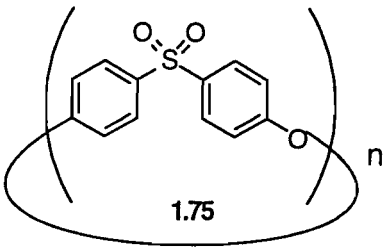
Scheme 1.25



1.73 **1.74**

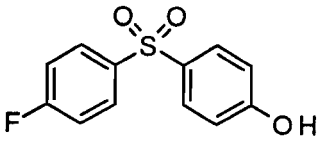
DMSO / Toluene, KOH, 130-5 °C
pseudo-high dilution condition
addition of reactants over 5 h

further reflux for 20 h
final product conc. = 21 mM



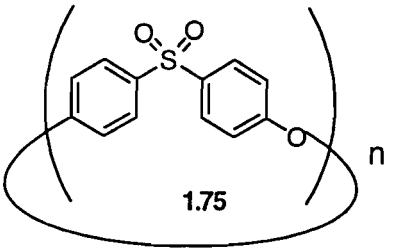
39 %

1.75



1.76

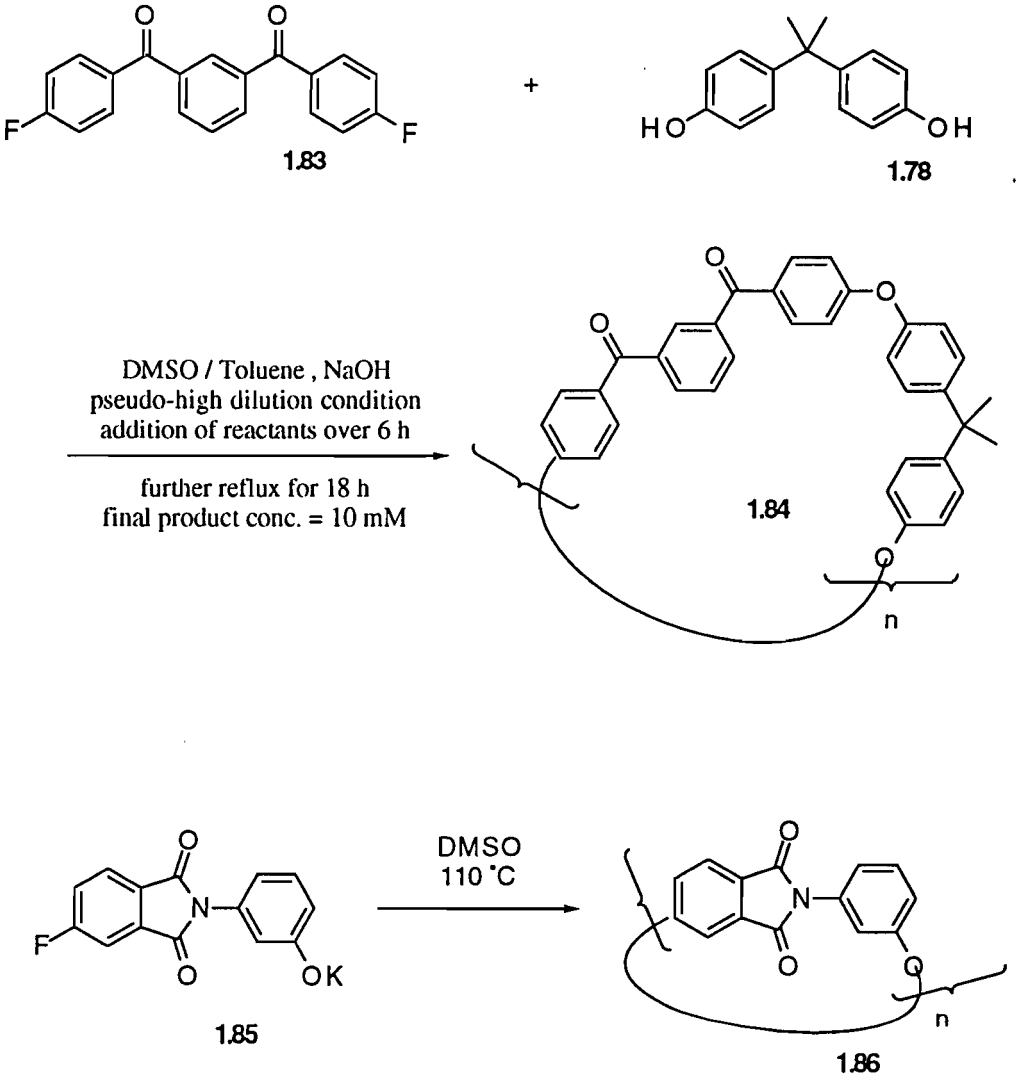
DMAc,K_2CO_3
130 - 140 °C, 3 days



1.75

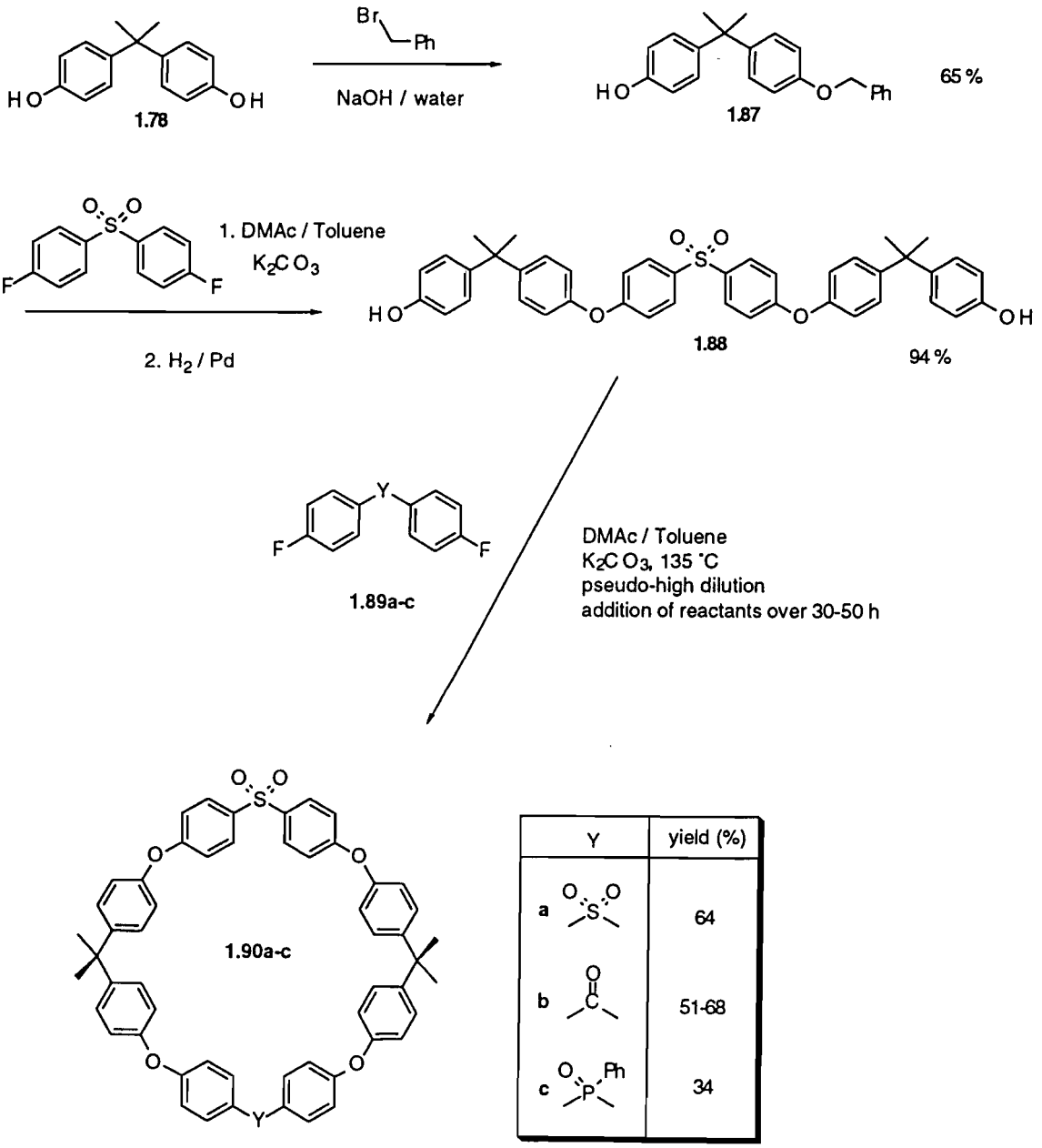
It was found that individual oligomers of the cyclic(ether sulfone) **1.75** have extremely high melting points (trimer, 447 °C, tetramer > 450°C). However, the crude mixture of cyclic oligomer is amorphous and begins to flow at about 230 °C. Melt

Scheme 1.27


F
F
1.83
+
HO
OH
1.78
DMSO / Toluene , NaOH
pseudo-high dilution condition
addition of reactants over 6 h
further reflux for 18 h
final product conc. = 10 mM
1.84
n
F
OK
1.85
DMSO
110 °C
n
1.86

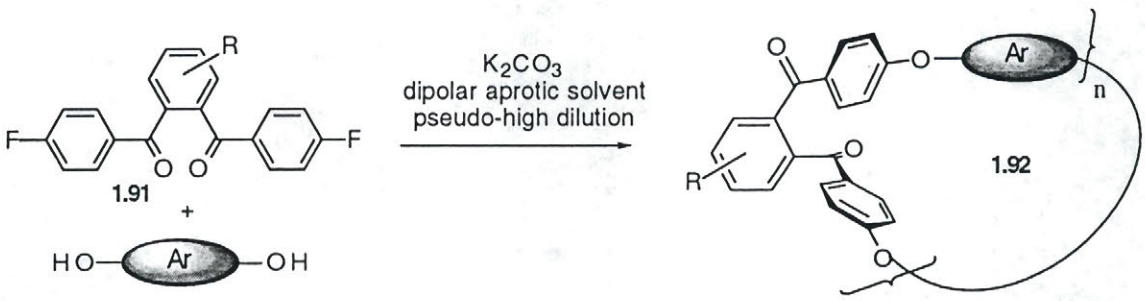
More recently, Gibson et al. reported the synthesis of a series of single sized cyclic(aryl ether)s **1.90** in a 4 step synthetic sequence in moderate to good yield (Scheme 1.28) [41,42] Their reported synthesis involves first the synthesis of the linear α,ω-dihydroxylarylether oligomer **1.88**. Condensation of this dihydroxyarylether **1.88** with various activated aromatic difluorides **1.89** using pseudo-high dilution conditions, yielded the desired macrocycles **1.90**. Typically, the reactants are added slowly over a period of 30 - 50 h. No polymerization study on these materials has been reported.

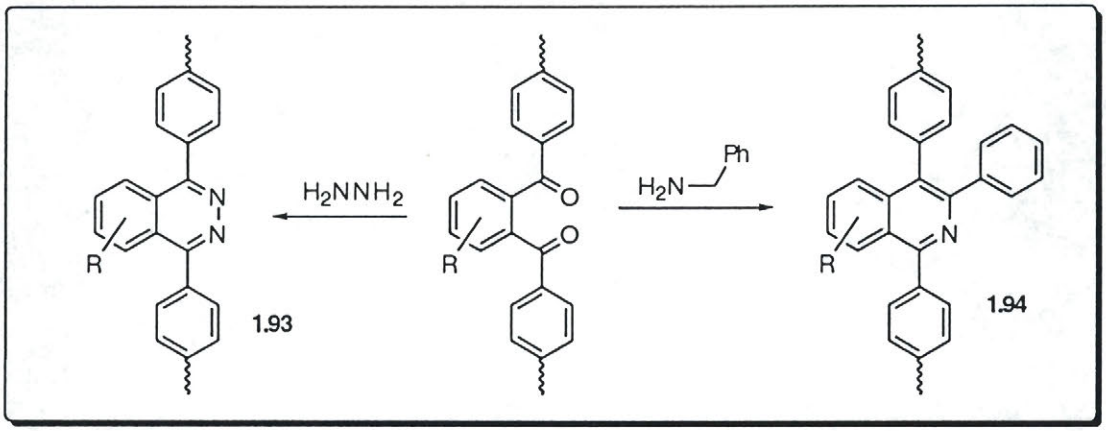
Scheme 1.28



1.4 Strategy and goals

The kind of cyclic materials that we proposed to synthesize contain a 1,2-dibenzoylbenzene moiety **1.92.** [43] They are expected to be relatively free of ring strain; therefore they should be relatively easy to make via a nucleophilic aromatic substitution reaction. Furthermore, the diketone moiety can be quantitatively transformed to a phthalazine **1.93** [44] or isoquinoline **1.94** moiety. [45]





Hence, we have a very easy way to obtain cyclic phthalazines and isoquinolines which would otherwise be difficult to obtain. Furthermore, transformation of the 1,2 - dibenzoylbenzene moiety to a phthalazine or isoquinoline should introduce considerable ring strain into the molecules because of the change in conformation. This may improve the polymerizability of the cyclic oligomers.

These cyclic oligomers would have low molecular weights and would have low melt viscosities. They would be expected to rapidly polymerize when heated in the presence of a nucleophile. The formation of polymer from the cyclic oligomers does not involve the evolution of any volatile by-products. The resulting high molecular weight linear polymers, which have been reported previously, are tough materials and have very high glass transition temperatures and thermooxidative stability. [43-45]

Hence, these cyclic oligomers should be attractive candidates as reactive intermediates for the synthesis of high performance polymers. Herein, studies on the synthesis and characterization of these cyclic(aryl ether ketone), cyclic(aryl ether phthalazine), and cyclic(aryl ether isoquinoline) oligomers will be discussed.

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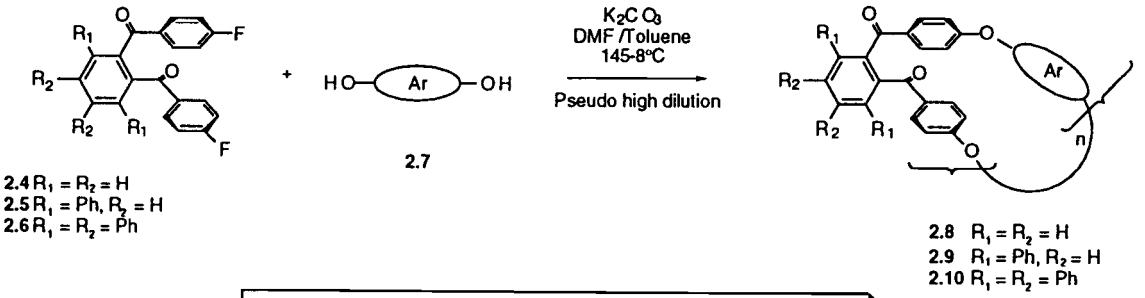
Chapter 2

Synthesis and Characterization of Novel Cyclic(aryl ether)s

2.1 Synthesis of cyclic(aryl ether ketone) oligomers containing the 1,2-dibenzoylbenzene moiety

Cyclic(aryl ether ketone)s containing a 1,2 -dibenzoylbenzene moiety were prepared by the aromatic nucleophilic substitution route utilizing a AA + BB approach, in which difluoro-monomers **2.4**, **2.5** & **2.6** were allowed to condense with bisphenols **2.7** to give the corresponding cyclic oligomers **2.8**, **2.9**, and **2.10** (Scheme 2.1 & Table 2.1). The difluoro-monomers **2.4**, **2.5** & **2.6** were prepared according to the reported method.[1]

Scheme 2.1



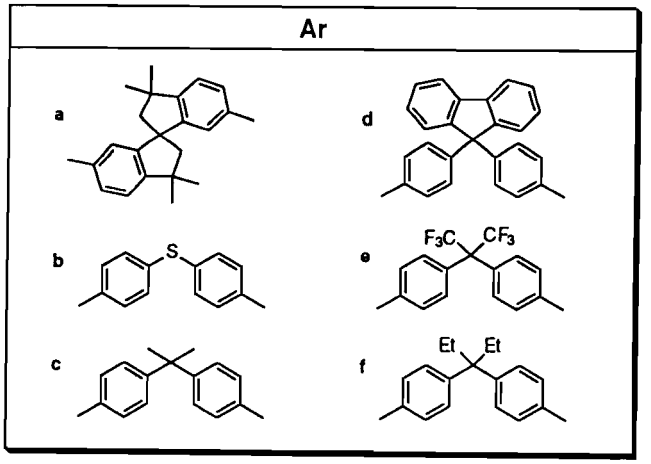


Table 2.1. Yields and molecular weights of cyclic(aryl ether ketone) oligomers.

Cyclic oligomer	Yield(%)[a]	M_w[b](kg/mole)	M_n[b](kg/mole)
2.8a	80	2.1	1.0
2.8b	90	3.1	1.3
2.8c	95	4.8	1.5
2.8d	80	5.1	1.7
2.9b	90	5.7	1.9
2.9c	80	5.3	1.9
2.9d	80	10.3	2.0
2.9e	95	5.8	1.7
2.9f	70	5.4	1.5
2.10b	36	11.6	1.8
2.22	80	11.4	0.5

[a] Isolated yield. [b] Measured by GPC and calibrated against polystyrene standard, M_w = weight average molecular weight, M_n = number average molecular weight.

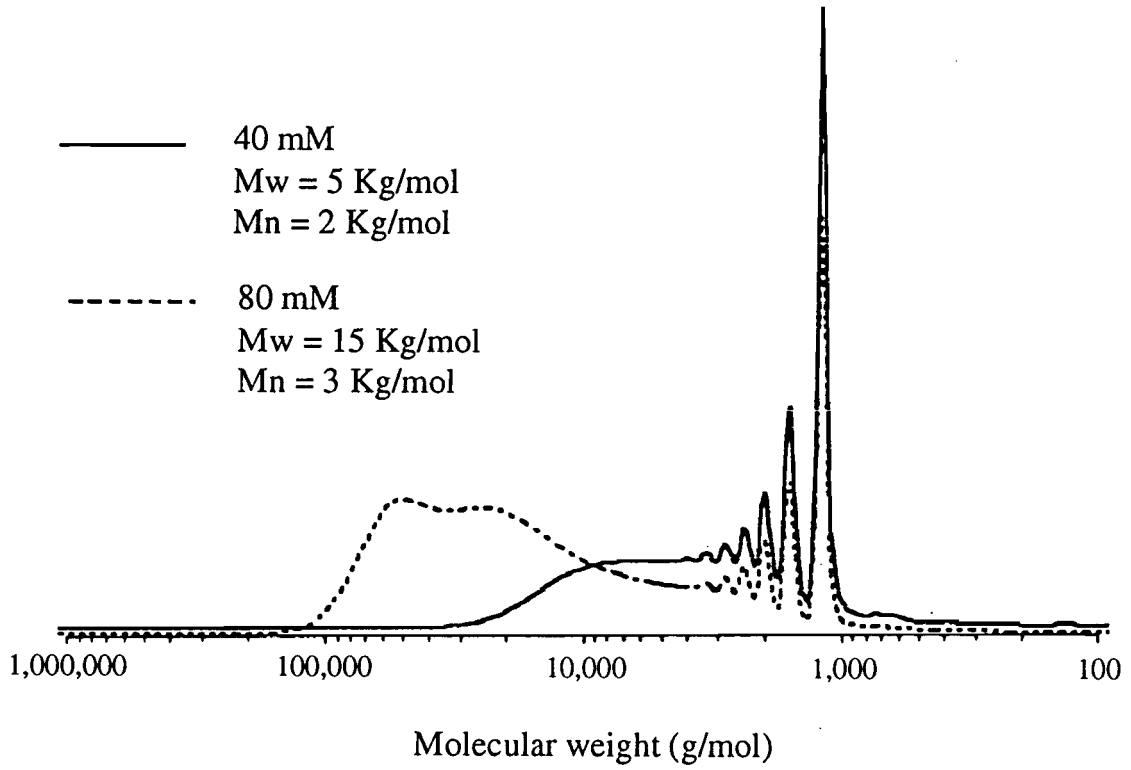
Pseudo-high dilution principle. Formation of cyclic oligomers is favored under dilute conditions; however, using a large volume of solvent would not be a viable approach. In order to achieve a practical synthesis of cyclic(ether ketone)s, a pseudo-high dilution principle [2] was used to achieve high yields of cyclic oligomers. Instead of using a large amount of solvent, a pseudo-high dilution condition can be created by slow controlled addition of the reactants into the reaction vessel at such rate that a steady low concentration of unreacted end-groups is maintained and, hence, favors the formation of cyclic oligomers even with a very high product concentration build up.

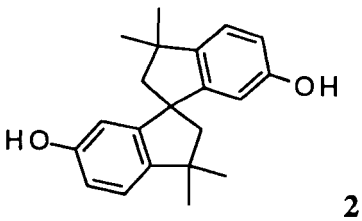
One critical factor in applying the pseudo-high dilution principle is the choice of the rate of addition of reactants, which is very much dependent on the rate of reaction. A general rule of thumb is that the higher the rate of reaction, the faster the rate of addition can be employed. Therefore, we used fluoro-monomers instead of their chloro-analogs because an aryl fluoride activated by a carbonyl or sulfone group in the *ortho* or *para* position is at least 100 times more reactive than an aryl chloride in aromatic nucleophilic substitution with phenoxide, [3] so that shorter addition times can be employed.

Thus, a concentrated N,N-dimethylformamide (DMF) solution of reactants (0.6M) is pumped into the reaction vessel containing solvent (DMF) and base (K_2CO_3) over a period of 8 h. The final concentration of the product can be as high as 40 mMolar. Toluene is used for continuous azeotropic removal of water generated during the reaction. The amount of toluene used is kept minimal, because its presence reduces the polarity of the solvent system and hence slows down the reaction rate. Following the addition of reactants, it takes another 8 h of reflux to ensure complete reaction.

When the final solution concentration is doubled to 80 mM, with the rate of addition unchanged, the high molecular weight fraction increases at the expense of the yield of cyclic oligomers. Gel permeation chromatographic (GPC) traces of cyclic oligomers **2.9c** obtained at two different concentrations illustrate this point (Figure 2.1). We generally employ K_2CO_3 as base; however, we found that using Cs_2CO_3 as base reduced the reaction time by half, from a total of 16 h to 8 h. Cesium phenoxide has been shown to have a higher reactivity than potassium phenoxide in these displacement reactions. [4]

Figure 2.1. GPC traces of cyclic oligomer **2.9c** at different final concentration.

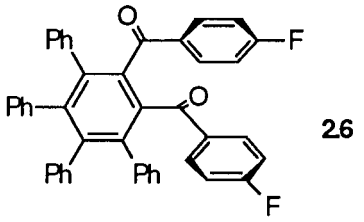




2.7a

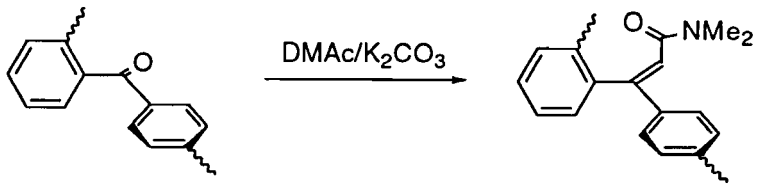
Formation of cyclic oligomers 2.8a from spirobiindanediol (SBI) 2.7a. When **2.7a** was used as the bisphenol to prepare cyclic oligomers **2.8a**, a high yield of cyclic materials was obtained without the use of the pseudo-high dilution condition as described above. A batch process was used and the concentration of the reaction mixture can be as high as 100 mM with a reaction time of 8 h. This can be explained in term of the 'bent' conformation of SBI, **2.7a** which promotes cyclic oligomers formation. [5]

Formation of cyclic oligomers 2.10 utilizing tetraphenyl substituted monomer 2.6. We encountered difficulty when trying to prepare cyclic oligomers from the tetraphenyl substituted monomer **2.6**. This monomer is not very soluble in polar aprotic solvents at room temperature. Hence, the high dilution conditions could not be employed in this case, and the yield of cyclic oligomer was comparatively low. The crude product was further purified by soxhlet extraction with ethyl acetate, to obtain low molecular weight cyclic oligomers.



2.6

Solvent effect and Aldol condensation side reaction. We found that use of N,N-dimethylacetamide (DMAc), N-methyl-2-pyrrolidinone (NMP) and dimethylsulfoxide (DMSO), in the preparation of cyclic oligomers from non-phenylated monomer **2.4**, failed to give a clean reaction. DMF was demonstrated to be the best solvent for formation of cyclic oligomers. We suspect that undesirable side reactions may have occurred between these solvents and the reactants or the oligomers formed. Based on matrix assisted laser desorption ionization - time of flight - mass spectrometry (MALDI-TOF-MS)[#] using $AgCF_3CO_2$ as cationization agent, and ^1H NMR analysis, we found that when DMAc was used as solvent an Aldol condensation reaction took place between the acidic α-methyl group of DMAc and the carbonyl groups of monomer **2.4** and the oligomers formed (eq. 2.1). We suspect that similar side reactions may also occur with NMP or DMSO. Since DMF does not have any acidic methyl group, the Aldol condensation side reaction was avoided.



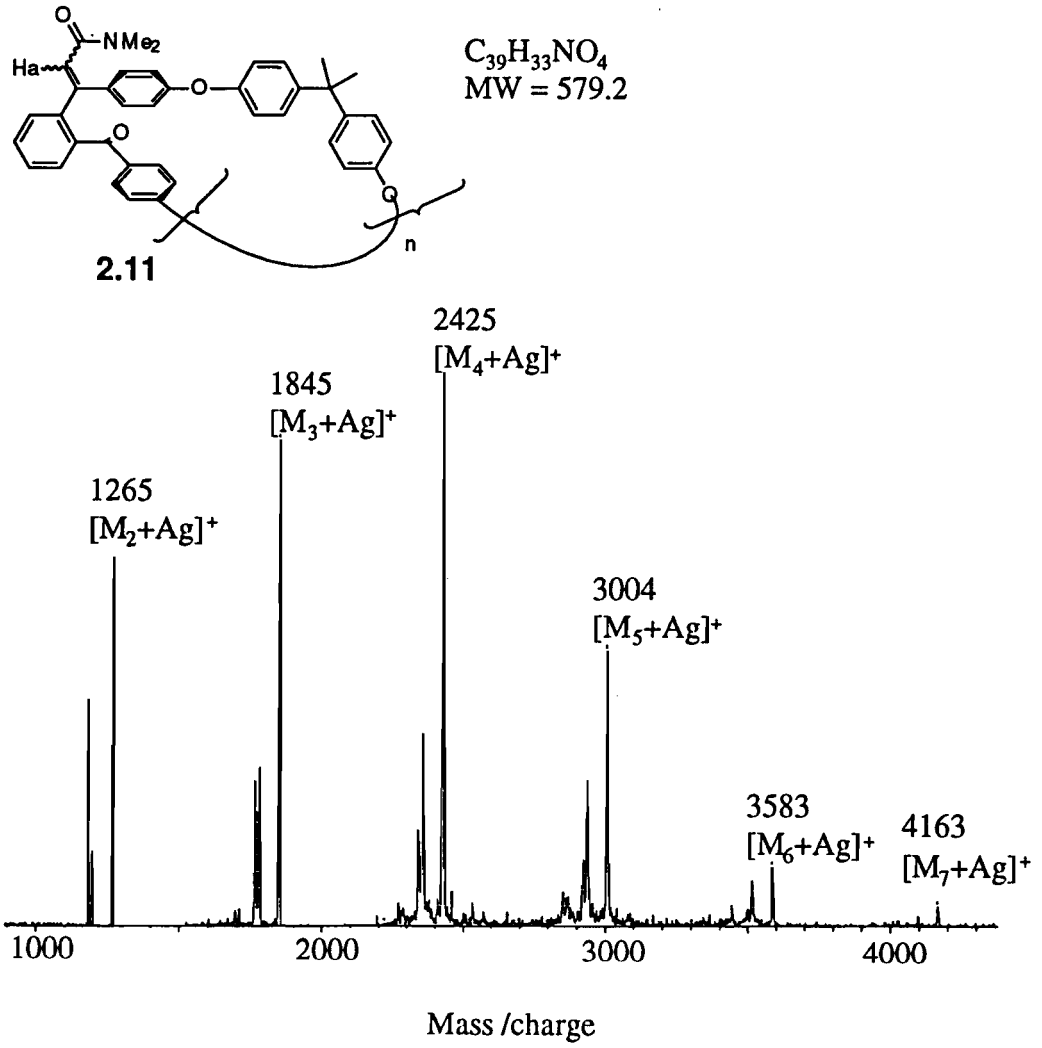
eq. 2.1

The MALDI-TOF-MS spectrum of the materials obtained from monomer **2.4** and bisphenol **2.7c**, using the cyclization procedure with DMAc as solvent is shown in Figure 2.2. Instead of giving the desired mass/charge (m/e) signals for cyclic oligomers, it gave

[#] Details of this technique will be discussed later in this chapter.

signals at 1265, 1845, 2425, 3004, 3583 & 4163 Da indicating the presence of oligomers which are Aldol condensation adducts **2.11** between oligomers and DMAc.

Figure 2.2. MALDI-TOF-MS spectrum of the materials obtained from monomer **2.4** and bisphenol **2.7c**, using DMAc as solvent.

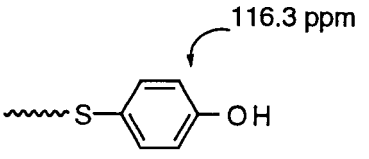


Examination of the ^{1}H NMR spectrum of the same materials revealed two pieces of important information indicating the presence of the condensation products **2.11** described above. The first one is the signals at 6.3 ppm which correspond to the olefinic proton (Ha) of the Aldol adduct **2.11**. The second one is signals in the region of 2.5 ppm to 3 ppm corresponding to the N-methyl proton of the Aldol adducts **2.11**. The integration is also consistent with one ketone group of the 1,2-dibenzoylbenzene moiety being condensed with DMAc per repeating unit.

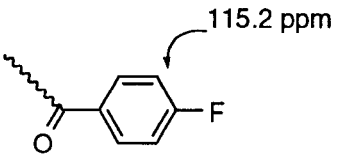
In our procedure, the reactants were influxed slowly into the reaction vessel containing solvent and base; therefore, this inevitably created a situation in which the oligomers formed were in contact with excess base, hence resulting in the formation of the Adol adducts. Furthermore, the electron-withdrawing effect of the adjacent carbonyl group in the 1,2-dibenzoylbenzene moiety increases the reactivity of the carbonyl group towards condenation reaction We found no problems in the preparation of cyclic oligomers from the diphenyl and tetraphenyl monomers **2.5** & **2.6** using DMAc as solvent. This may be due to the fact that the extra phenyl substitutents create a steric barrier and make the ketone group less accessible.

Cyclic nature of the oligomers. The low concentration of end groups detected and the low molecular weight of the materials formed supported the formation of cyclic oligomers. Direct evidence of their cyclic nature was obtained from the mass spectra of the materials prepared.

For example, the GPC trace of the cyclic oligomer **2.8b** shows that it is a low molecular weight material with number average molecular weight M_n ~1500 g/mol. This implies an average degree of polymerization (*DP*)~ 3. However, examination of the ^{13}C NMR spectrum (Figure 2.3) shows that no obvious signals from the possible fluoro and phenolic end groups **2.12** and **2.13** are detected. Aromatic carbons ortho to the hydroxy and fluoro groups would give very characteristic up-field signals in the region of 116 and 115 ppm, respectively. [6] The use of more sensitive nuclei such as ^{19}F make it possible to detect the presence of end group **2.13** which gives rise to signals in the region of -103-7 ppm. (Figure 2.4) Fluorobenzene was used as internal standard, and the concentration of the end groups **2.13** was determined to be one in every 300 structural repeating units in the case of **2.8b**.



2.12



2.13

With the advance of soft ionization techniques, especially matrix assisted laser desorption ionization (MALDI), the accessible mass range of mass spectrometry has been extended considerably. The use of MS as a rapid and accurate method for the detection and identification of complex polymeric mixtures would be of great interest to polymer chemists. Information such as absolute molecular weight distribution, sequence of the repeating units, polymer impurities, and structural information can be obtained. [7]

Figure 2.3. (i) ^{13}C NMR (125 MHz, $CDCl_3$) of cyclic oligomer **2.8b**, (ii) ^{13}C NMR of corresponding linear polymer of **2.8b**, (iii) & (iv) expansions of ^{13}C NMR of cyclic oligomer **2.8b.**

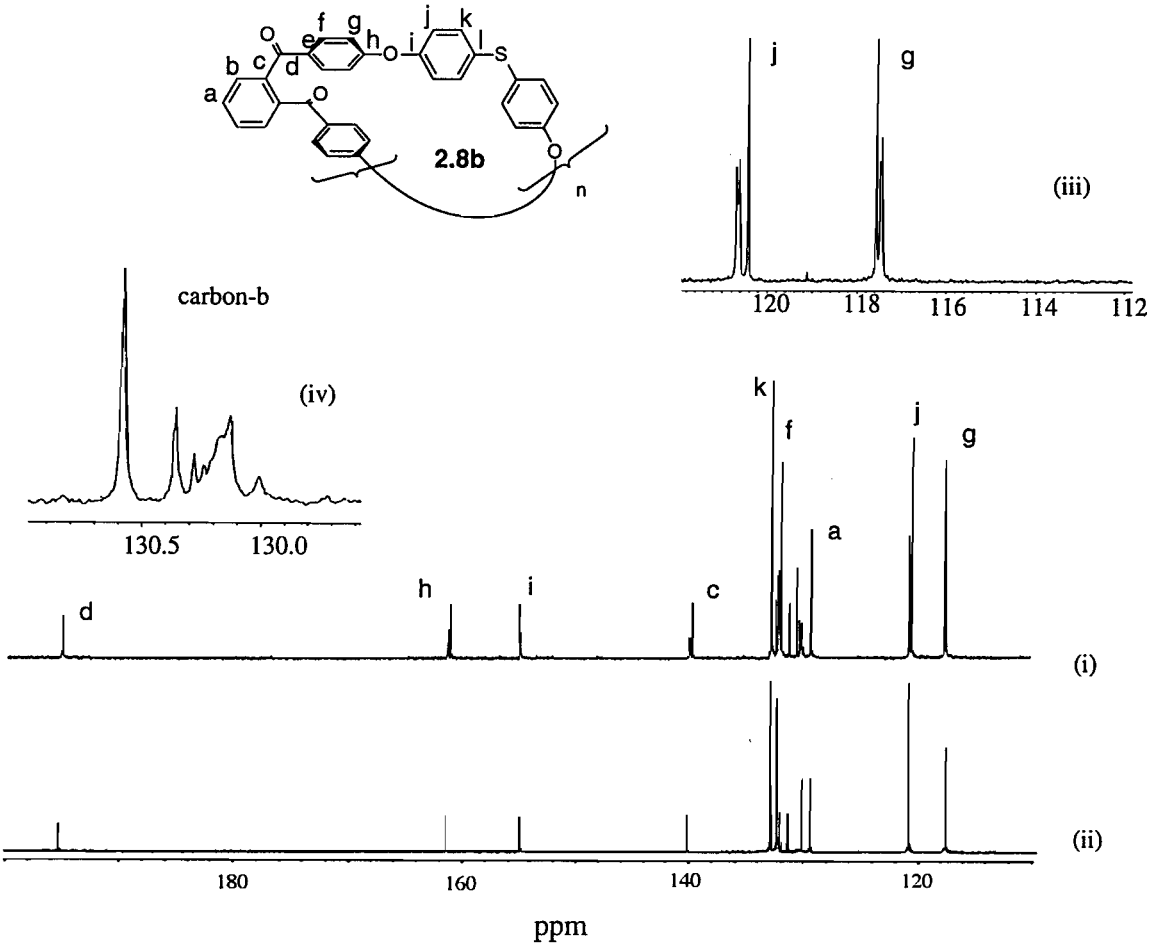
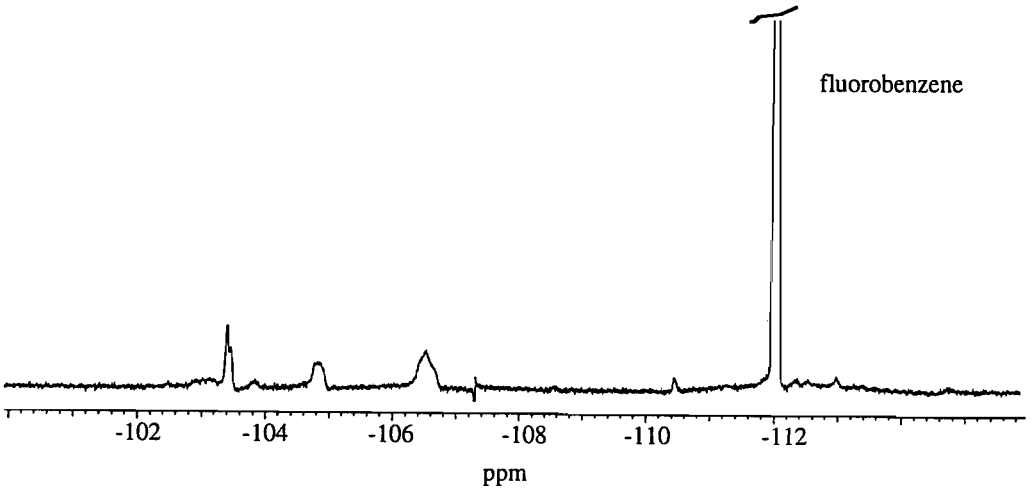


Figure 2.4. ^{19}F NMR(500MHz, $CDCl_3$) of cyclic oligomer **2.8b**.

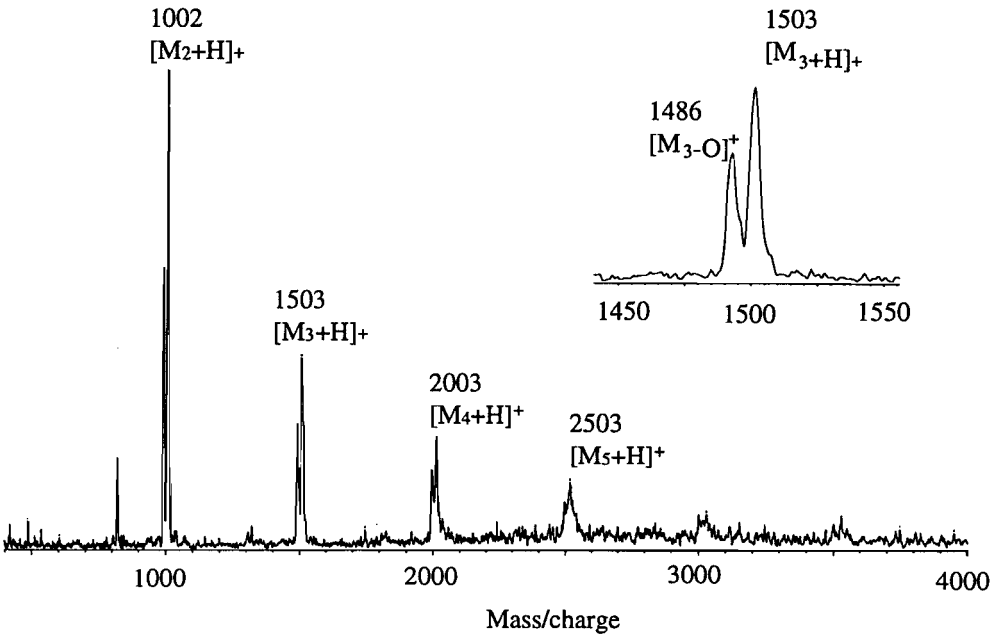


In MALDI, the samples to be analyzed are mixed uniformly with a substance called a matrix. In an environment where excess matrix is present, the minute sample crystals are surrounded by the matrix crystals (or in an amorphous state). The matrix which has resonance absorption at the laser wavelength, absorbs the laser energy and causes rapid heating of the matrix for the sample to be vaporized.

Reports of the use of this technique for the analysis of polyacrylamide [8], polyhydroxyalkanoates [9], polystyrene and poly(ethylene glycol)s have appeared recently. [7] We found that MALDI-TOF-MS is a simple and rapid method for the detection and identification of oligomeric aryl ethers.

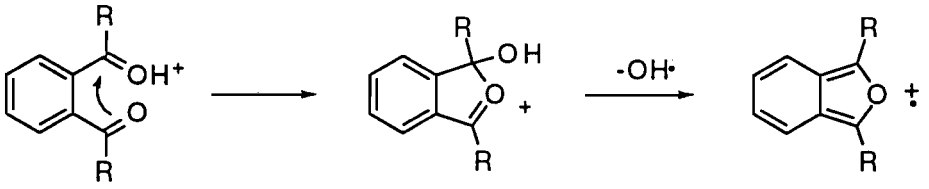
The MALDI-TOF-MS spectrum of **2.8b**, using 2,5-dihydroxybenzoic acid (gentisic acid) as the matrix material, gives the correct molecular ion peaks for the desired cyclic oligomers, up to pentamer (n=5), with reasonable signal to noise ratio. (Figure 2.5a & Table 2.2a)

Figure 2.5a. MALDI-TOF-MS spectrum of **2.8b** using gentisic acid as matrix.



The expanded scale of the MS spectrum of **2.8b** shows two signals for each oligomer. For example, signals for the cyclic trimer are located at 1486, and 1503 Da. The signal at 1503 Da corresponds to the protonated molecular ion $[M+H]^+$ peak, and the signal at 1486 Da is due to loss of oxygen through intramolecular cyclization of trimer of **2.8b** to form isobenzofuran (eq. 2.2). The loss of an oxygen is observed in all other samples containing the 1,2-dibenzoylbenzene moiety. This kind of fragmentation was

observed not only in the MALDI method but also in fast atom bombardment (FAB) ionization. We have also observed signals for the potassium adduct $[M_X+K]^+$ and sodium adduct $[M_X+Na]^+$ together with $[M_X+H]^+$ ion signals in the MALDI-TOF mass spectra of other oligomers.



eq. 2.2

Table 2.2a. MALDI-TOF-MS data of cyclic oligomer **2.8b** using gentisic acid as matrix.

Signal(m/e)	Rel. Intensity(%)	Assignment[a]	Calculated m/e	Deviation (Da)[b]
985	60	M_2-O	985	0
1002	100	M_2+H	1002	0
1486	25	M_3-O	1486	0
1503	40	M_3+H	1503	0
1986	16	M_4-O	1986	0
2003	22	M_4+H	2003	0
2503	15	M_5+H	2504	- 1

[a] M_x represent the molecular ion with x repeating units, average molecular weight calculated for repeating unit $C_{32}H_{20}O_4S$ = 500.6, [b] deviation = experimental value - calculated value.

More recently, we find that using 1,8,9-anthracenetriol (dithranol) as matrix and $AgCF_3CO_2$ as cationization agent gives MS spectra with better signal to noise ratio. For example, the MALDI-TOF-MS spectrum of cyclic oligomer **2.8b** using these two reagents gives the correct molecular ion signals for the desired oligomers and silver adduct $[M_X+Ag]^+$, up to octamer (n=8), with excellent signal to noise ratio (Figure 2.5b & Table 2.2b). The fragmentation process as shown in equation 2.2 is also suppressed to give a very simple spectrum.

Figure 2.5b. MALDI-TOF-MS spectrum of **2.8b** using dithranol as matrix and $AgCF_3CO_2$ as cationization agent.

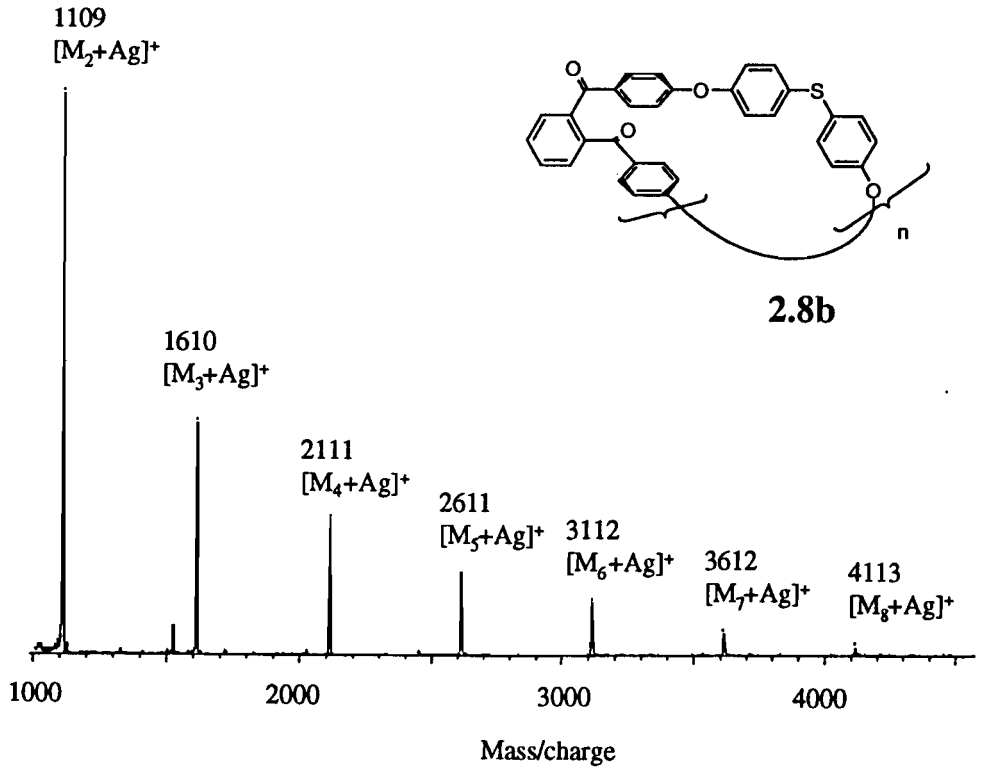


Table 2.2b. MALDI-TOF-MS data of cyclic oligomer **2.8b** using dithranol as matrix and $AgCF_3CO_2$ as cationization agent.

Signal(m/e)	Rel. Intensity(%)	Assignment[a]	Calculated m/e	Deviation (Da)[b]
1109	100	M_2+Ag	1109	0
1610	37	M_3+Ag	1610	0
2111	19	M_4+Ag	2110	+1
2611	11	M_5+Ag	2611	0
3112	7	M_6+Ag	3111	+1
3612	3	M_7+Ag	3612	0
4113	0.5	M_8+Ag	4112	+1

[a] M_x represent the molecular ion with x repeating units, average molecular weight calculated for repeating unit $C_{32}H_{20}O_4S$ = 500.6, [b] deviation = experimental value - calculated value.

Isolation of a discrete cyclic oligomer. We have isolated the 46 member cyclic dimer **2.8b (n=2).** The dimer can be easily isolated from the crude mixture of oligomers by crystallization using benzene as solvent. Interestingly this dimer **2.8b(n=2)** can form (1:1) inclusion compounds [10] with organic solvents such as benzene, ethyl acetate and DMF.

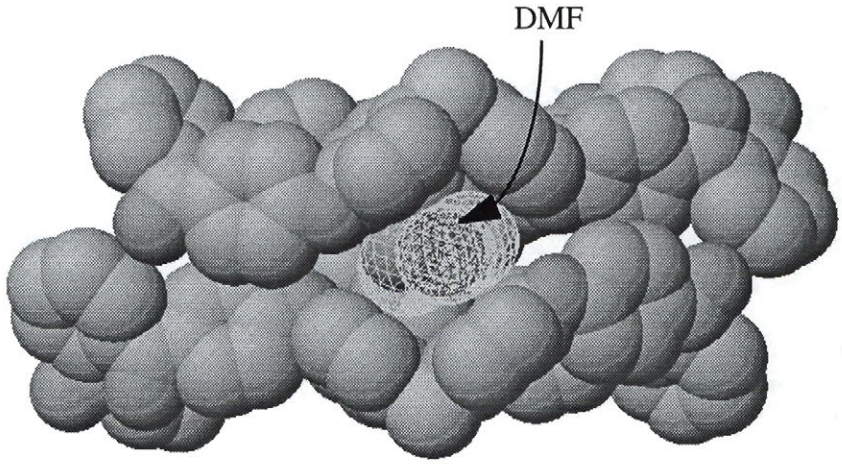
This finding is based on thermogravimetric analysis (TGA) and ^{1}H NMR studies on the crystals of **2.8b(n=2)** obtained from these solvents. These inclusion compounds are stable under vacuum drying at 100 °C. All three inclusion compounds release their included solvent guest at a temperature much higher then the boiling point of the corresponding solvents (Table 2.3).

Table 2.3. Thermal stability of inclusion compound of cyclic dimer **2.8b(n=2).**

Solvent guest	Thermal dec. (°C)[a]	Bp (°C)[b]	Difference(°C)[c]
ethyl acetate	166	77.5	+88.5
benzene	125	80	+45
DMF	175	153	+22

[a] The temperature onset for the evolution of the solvent as determined by TGA at a rate of 20 °C/min under nitrogen atmosphere. [b] The boiling point of the solvent guest at atmospheric pressure. [c] Difference between the decomposition point of the inclusion compound and the boiling point of the solvent guest.

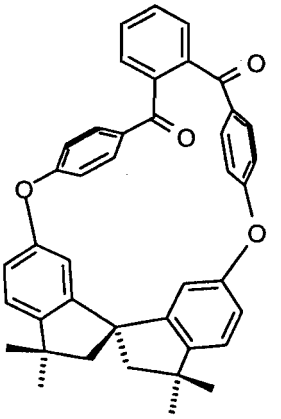
Figure 2.6. X-ray crystal structure of cyclic dimer **2.8b(n=2)** with DMF.



In order to determine whether the solvent inclusion is in the extramolecular cavities (clathrate formation) or intramolecular cavities,[10] we used X-ray crystallographic method. The X-ray crystal structure of **2.8b(n=2)** was determined from a crystal obtained by crystallization from DMF (Figure 2.6). It is found that **2.8b(n=2)** adopts a flattened structure with the 1,2-dibenzoylbenzene moiety assuming a carbonyl *cis* conformation. Furthermore, **2.8b(n=2)** forms stable clathrate with DMF in which stoichiometric

amounts of the DMF molecule are trapped in the lattice void created by two 4,4'-thiodiphenyl fragments from two different molecules of **2.8b(n=2)** that are stacked together.

Composition of the cyclic oligomers. Analyses base on GPC and HPLC indicate that the reaction generates a mixture of oligomeric cyclic(aryl ether ketone)s. The range of oligomerization is principally from degree of polymerization of 2 up to 10. A typical mixture contains 38 wt % cyclic dimer, 16 wt % trimer, 10 wt % tetramer, 7 wt % pentamer, 4 wt % hexamer, and 25 wt % higher homologues. On the other hand, oligomer **2.8a** contains 37 wt % of cyclic monomer (n=1). As we have mentioned earlier, the special 'bent' configuration of SBI not only facilitates cyclization, but also favors the formation of cyclic monomer in high yield as indicated by GPC and MS results. The formation of cyclic monomer was not observed when other bisphenols were used.



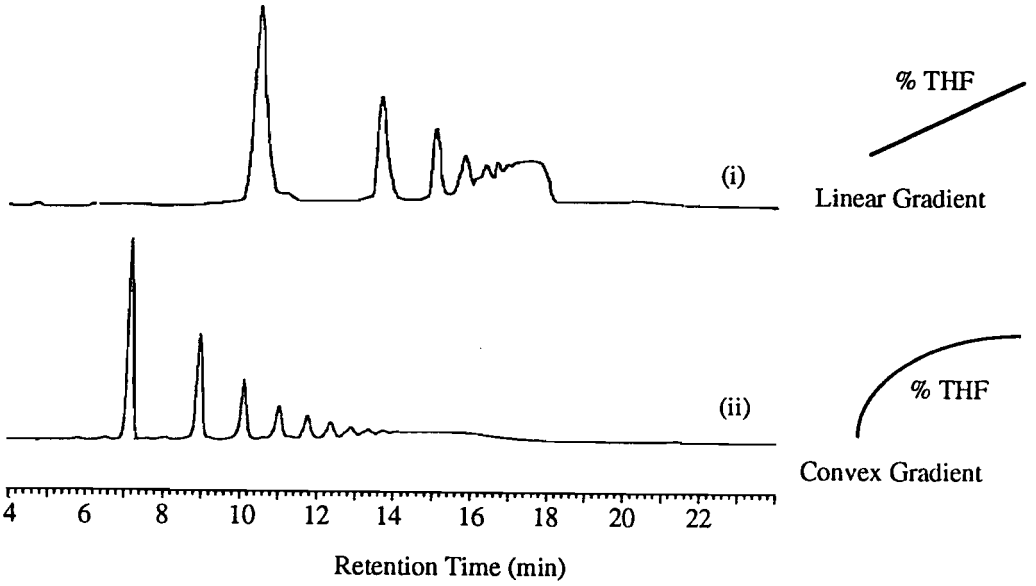
2.8a(n=1)

Reverse phase HPLC with the appropriate choice of stationary phase, solvents combination, and gradient program is found to be a very useful method to achieve a better separation of the individual oligomers of cyclic mixture. [11] It gives more precise information on the composition of the cyclic oligomers compared to the use of GPC. In the case of GPC, in order to resolve the individual oligomers in the mixture, three 500 Å column in series have to be used. [12]

In the HPLC analyses, a combination of a thermodynamically good solvent (THF), and a thermodynamically poor solvent (water) was used. The gradient program was started with a combination of two solvents (60% of THF, 40% of water) and the volume fraction of THF gradually increased to 85% and this results in a good separation of the oligomers. We found that oligomers with molecular weight up to 5,000 can be separated. The use of a linear gradient results in peaks at the high molecular weight region compressed together (Figure 2.7) resulting in more than enough separation at the beginning, but inadequate resolution at the end of the chromatograph. A better separation can be achieved using a

convex gradient, in which the volume percentage of THF increases more rapidly at the beginning and levels off when approaching the end of the program.

Figure 2.7. HPLC traces of cyclic oligomer **2.9b** (i) linear gradient; (ii) convex gradient.



^{13}C NMR of the materials also provides information on the composition of materials. It was found that in the series of cyclic oligomers **2.8**, carbons on the diketone moiety are sensitive to the size of the oligomers. For example, using carbon-b of cyclic oligomer **2.8b,** one can differentiate signals from dimer up to pentamer (Figure 2.3iv).

According to the theory of macrocyclization of condensation polymers developed by Jacobson and Stockmayer (JS theory),[13] the distribution of cyclic species obeys the following equation, which assumes that the distribution of the polymer end-to-end distances in a randomly coiled polymer is given by a Gaussian function.

$$C_n = Bn^{-\gamma}x^n$$

C_n is the concentration of cyclic oligomer with degree of polymerization of n, x is the fraction of reacted end groups of the chains. B is a constant depending on the chemical nature of the molecule and the solvent. For a very high extent of reaction in a system x will approach unity. Therefore, a plot of $\ln(C_n)$ vs. $\ln(n)$ will result in a linear line, with slope of $-\gamma$, where $\gamma = 2.5$, according to JS theory prediction.

Table 2.4. Weight percent (W_n) and concentration of cyclic oligomers.

	2.8b (influxion method)[a]		**2.8c (influxion method)[a]**	
n	W_n(%)	C_n(mM)	W_n(%)	C_n(mM)
2	47.5	9.5	47.7	9.5
3	21.2	2.8	20.8	2.8
4	10.4	1.0	10.7	1.1
5	5.5	0.4	5.9	0.5
6	3.4	0.2	4.1	0.3
γ	3.4		3.3	

	2.9b (influxion method)[a]		**2.9b (batch method)[b]**	
n	W_n(%)	C_n(mM)	W_n(%)	C_n(mM)
2	38.7	7.7	26.2	5.2
3	21.8	2.9	13.6	1.8
4	12.1	1.2	9.5	1.0
5	6.8	0.5	7.2	0.6
6	5.1	0.3	5.2	0.4
γ	2.9		2.4	

[a] The experimental conditions for the influxion method is the same as the general synthesis of cyclic oligomer in the experimental section. [b] The same conditions as the influxion method, except all the reactants were added to the reaction vessel at the beginning of the reaction, and it was allowed to reflux for 18 h to reach ring-chain equilibrium.

Based on the weight percent of the oligomers obtained by HPLC analyses, we calculated the C_n for each degree of polymerization (Table 2.4). We found that good linear plots were obtained for the oligomers. Some examples of the results are shown in Figure 2.8 & 2.9. The γ values for our system are higher than 2.5. This indicates that the yields of cyclic oligomers apparently decrease upon increasing molecular weight more rapidly than predicted by JS theory. We believe that the high value of γ compared to that predicted by Jacobson and Stockmayer may due to the fact that an influxion method, instead of a batchwise procedure, was used for the preparation of the cyclic oligomers. Hence the creation of the pseudo-high dilution condition may favor the formation of smaller ring size cyclic oligomers as a result of dilution beyond critical concentration as suggested by JS theory. An experiment was carried out to prepare cyclic oligomer **2.9b** by a batch process for an extended period (18 h) so that ring chain equilibrium was allowed to build up, in order to satisfy the conditions in the JS theory (Table 2.4). In this case we obtain a value γ = 2.4 which is in good agreement with the JS theory within experimental error (Figure 2.9).

Figure 2.8. Plot of ln(*Cn*) against ln(*n*) of cyclic oligomers **2.8b** and **2.9b** obtained by influxion method.

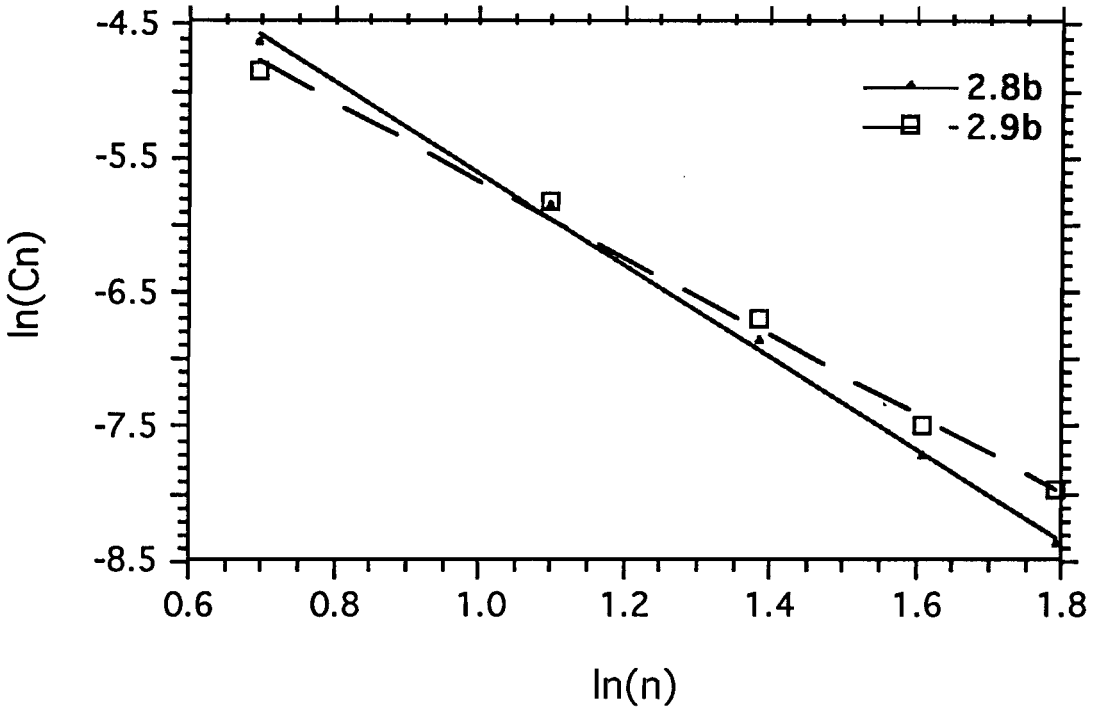
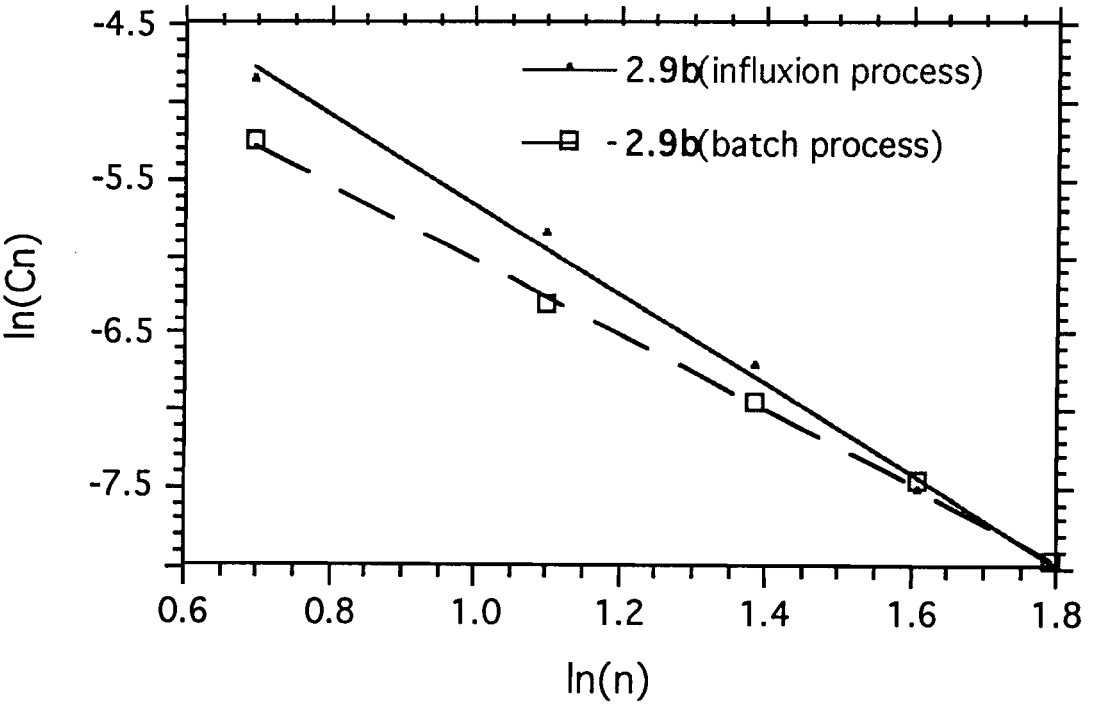


Figure 2.9. Plot of ln(*Cn*) against ln(*n*) of cyclic oligomer **2.9b** obtained by a influxion method and a batch method.



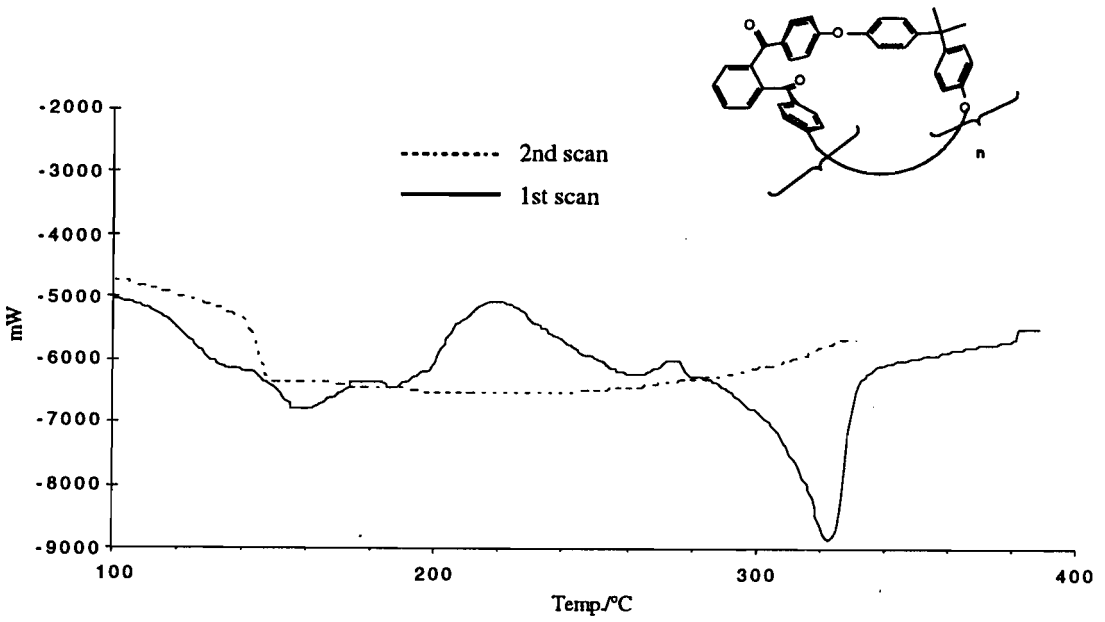
Thermoanalyses of cyclic(ether ketone) oligomers. The glass transition temperature (Tg) and melt temperature (Tm) of the cyclic oligomers were determined by differential scanning calorimetry (DSC) at a heating rate of 20 °C per min. (Table 2.5). It was found that most of the cyclic oligomers are crystalline. Usually, for the first scan, a heat of crystallization was observed, followed by the Tm. For example, a DSC trace of cyclic oligomer **2.8c** is shown in Figure 2.10. It was found that the Tg of the cyclic oligomers are in general 10 - 20 °C lower than the corresponding linear high molecular weight polymer. It is known that the corresponding linear high molecular weight polymers are amorphous. [1] The detection of Tm in most of the cyclic oligomers may be attributed to the fact that a high weight percentage of cyclic dimers are present in the oligomeric mixture, and these dimers crystallize readily.

Table 2.5. Thermoanalyses of cyclic oligomers.

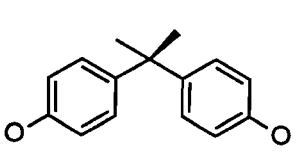
Cyclic oligomer	Tg (°C) [a]	Tm (°C) [a]	TGA (°C) [b]
2.8a	186 (197)	350	481
2.8b	142 (156)	234	476
2.8c	157 (180)	324	452
2.8d	220 (240)	n.d.[c]	517
2.9b	189 (198)	388	462
2.9c	194 (221)	>450	480
2.9d	254	n.d.[c]	479
2.9e	200	365	526
2.9f	177	412	483
2.10b	218	395	452
2.22	222(234)	415	450

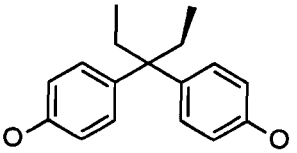
[a] Measured on DSC under nitrogen atmosphere (50 mL/min), heating rate was 20°C/min, number in bracket is the Tg of the corresponding high molecular weight linear polymer. [b] Reported 5% weight loss under nitrogen atmosphere (200 mL/min), heating rate was 20°C/min. [c] n.d. = Not detected.

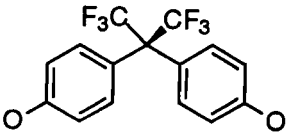
Figure 2.10. DSC traces of cyclic oligomer **2.8c**.



It was found that the diphenyl substituted cyclic oligomers **2.9** have very high Tms. For instance, **2.9c** has a Tm above 450 °C and this cyclic oligomer is relatively insoluble in chloroform. However, replacement of the BPA moiety with the BPP moiety, which has a flexible diethyl group, results in cyclic oligomers **2.9f**, in which Tm is lowered down to 412 °C, and it is readily soluble in chloroform. Replacing the BPA moiety in **2.9c** with the hexafluoro-BPA moiety results in cyclic oligomer **2.9e**. It has a Tg comparable to **2.9c** but the Tm is dramatically reduced to 363 °C, and it is readily soluble in chloroform.


BPA

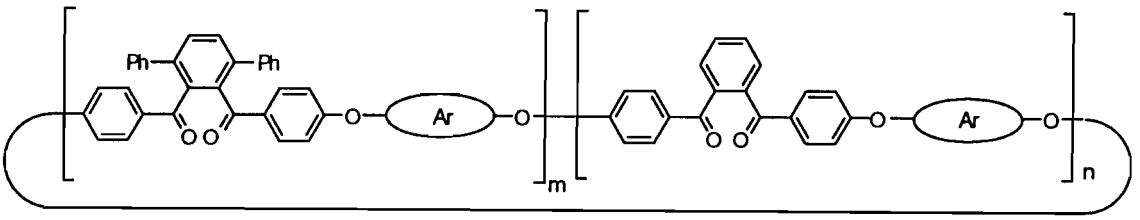

BPP



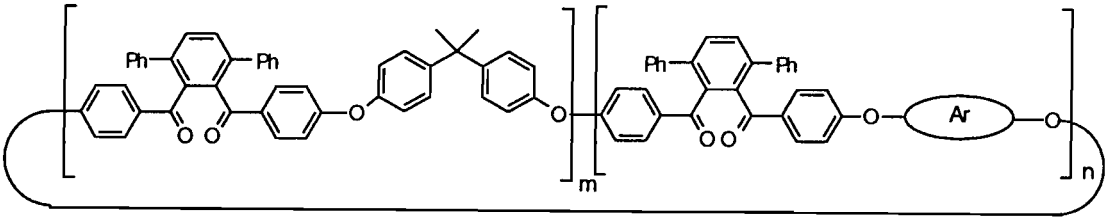
Hexafluoro-BPA

Synthesis of random co-cyclic oligomers. We found that some of these cyclic materials are highly crystalline and have high Tms. The high melting temperature of these cyclic oligomers would be a handicap from a processing point of view. One possible way to reduce the crystallinity and reduce the Tm of the cyclic materials is to prepare random co-cyclic oligomers. For example, we applied the same synthetic conditions as in the preparation of the homo-cyclic oligomers, and prepared random co-cyclic oligomers **2.14**, **2.15** and **2.16** by condensing bisphenols with a mixture of difluoro-monomers **2.4** and

2.5 in various proportions (Table 2.6). Random co-cyclic oligomers **2.17**, **2.18** and **2.19**, were also prepared from difluoro-monomer **2.5** with a mixture of two bisphenols (Table 2.7). All random co-cyclic materials, except **2.19**, were found to be amorphous. In the case of **2.19**, crystallinity was found, but the Tm was lower than the homo-cyclic oligomers **2.9c** and **2.9e.**



2.14, 2.15 & 2.16



2.17, 2.18, & 2.19

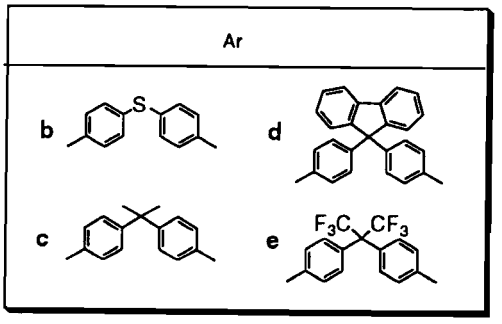


Table 2.6. Yields, molecular weight and thermoanalyses of random co-cyclic oligomers by mixing two kinds difluoro-monomers **2.4** & **2.5**.

Cyclic oligomer	Ar	m:n	Yield(%)[a]	M_w [b]	M_n [b]	Tg (°C) [c]	Tm(°C) [c]	TGA(°C) [d]
2.14	b	1:1	85	4.8	1.5	169	n.d. [e]	455
2.15	b	3:1	85	4.0	1.3	180	n.d. [e]	475
2.16	c	1:1	85	5.4	1.4	180	n.d. [e]	473

Table 2.7. Yields, molecular weight and thermoanalyses of random co-cyclic oligomers by mixing two kinds of bisphenols.

Cyclic oligomer	Ar	m:n	Yield(%)[a]	M_w [b]	M_n [b]	Tg (°C) [c]	Tm(°C) [c]	TGA(°C) [d]
2.17	b	1:1	85	8.5	1.5	195	n.d. [e]	450
2.18	d	1:1	95	6.2	1.7	219	n.d. [e]	461
2.19	e	1:1	95	6.8	1.7	201	354	528

[a] Isolated yield. [b] Measured by GPC and calibrated against polystyrene standard, unit in kg/mole. [c] Measured on DSC under nitrogen atmosphere (50 mL/min), heating rate was 20°C/min. [d] Reported 5% weight loss under nitrogen atmosphere (200 mL/min), heating rate was 20°C/min. [e] n.d. = Not detected

A HPLC of random co-cyclic oligomers **2.14** is shown in Figure 2.11. Early members of the cyclic mixture can be identified by comparing with HPLC traces of cyclic oligomers **2.8b** and **2.9b**. The MALDI-TOF-MS of **2.14** is shown in Figure 2.12. The upper detection limit is low compared to that for the homo-cyclic materials. Only signals up to trimer have reasonable signal to noise ratio. This is attributed to the fact that the co-cyclic mixture contains more oligomeric components than the homo-cyclic mixture. For example, in the case of **2.14**, the number of possible combinations of cyclic oligomeric components with n-repeating units is equal to n+1. Hence, there will be three molecular ion signals for the dimer, and four for the tetramer, and so on. The total available charge produced during MALDI will be distributed over a very large number of different ions, hence lead to the low upper detection limit for co-cyclic materials. The formation of both potassium and sodium adducts complicates the situation even more.

Figure 2.11. HPLC traces of cyclic oligomers (i) **2.8b**, (ii) **2.9b** & (iii) random co-cyclic **2.14**; A_xB_y indicates a cyclic (x+y)mer component with x repeating units of A, and y repeating units of B.

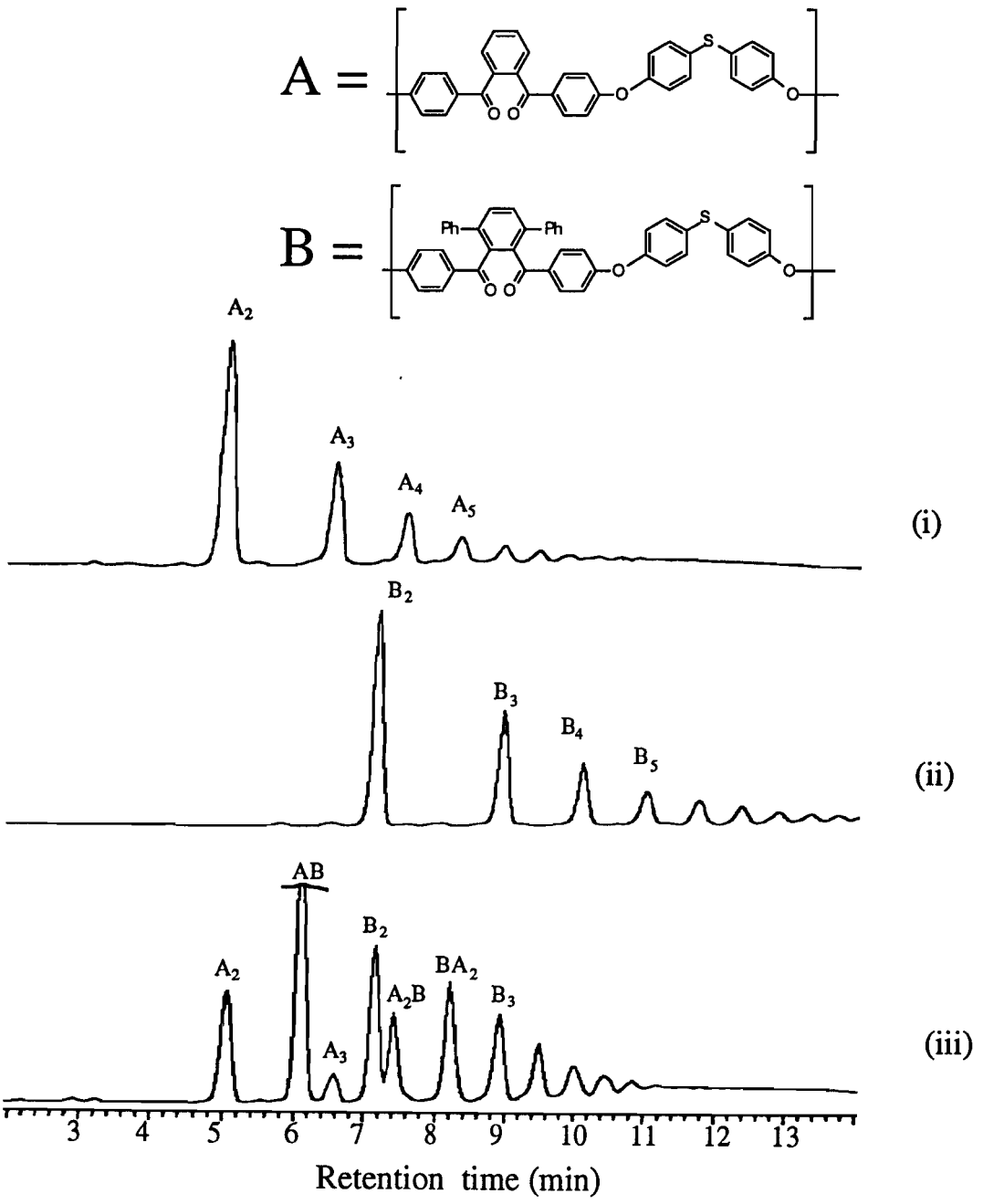
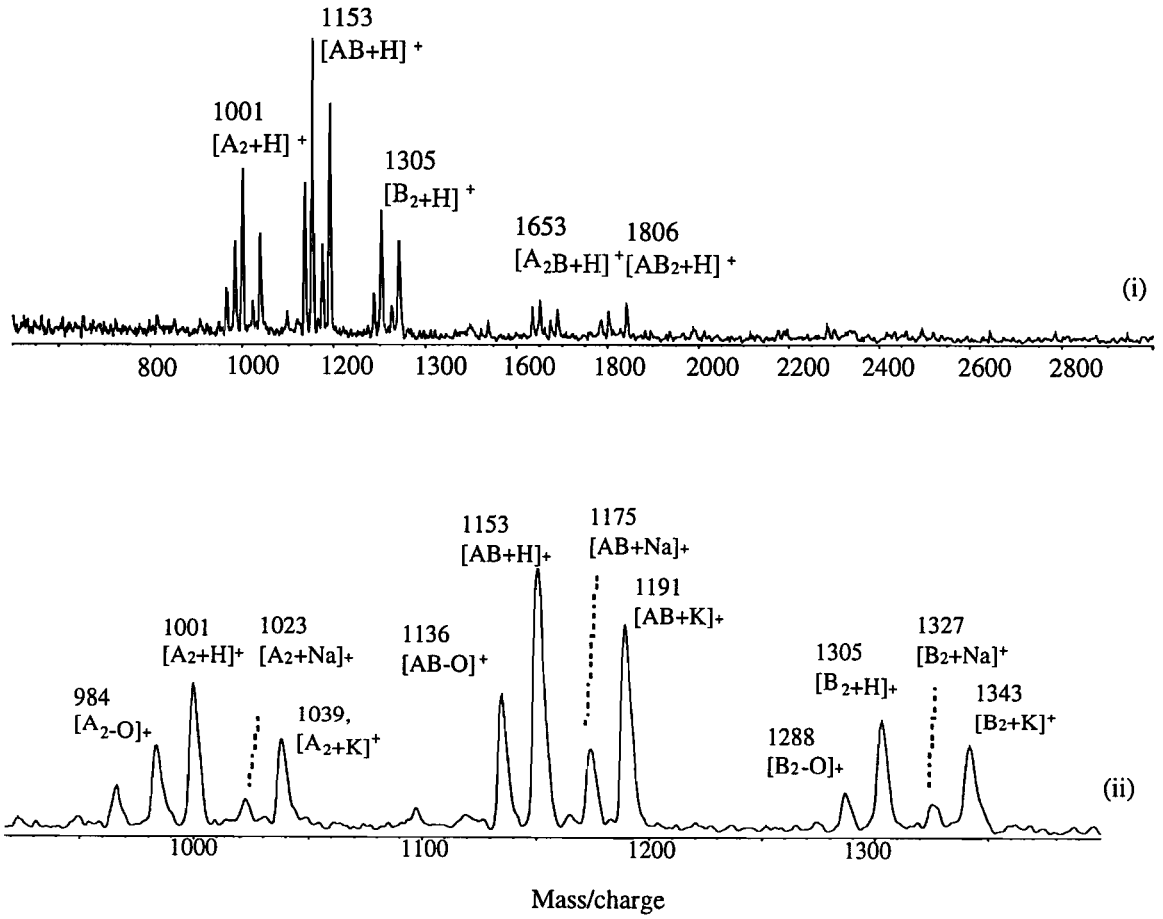
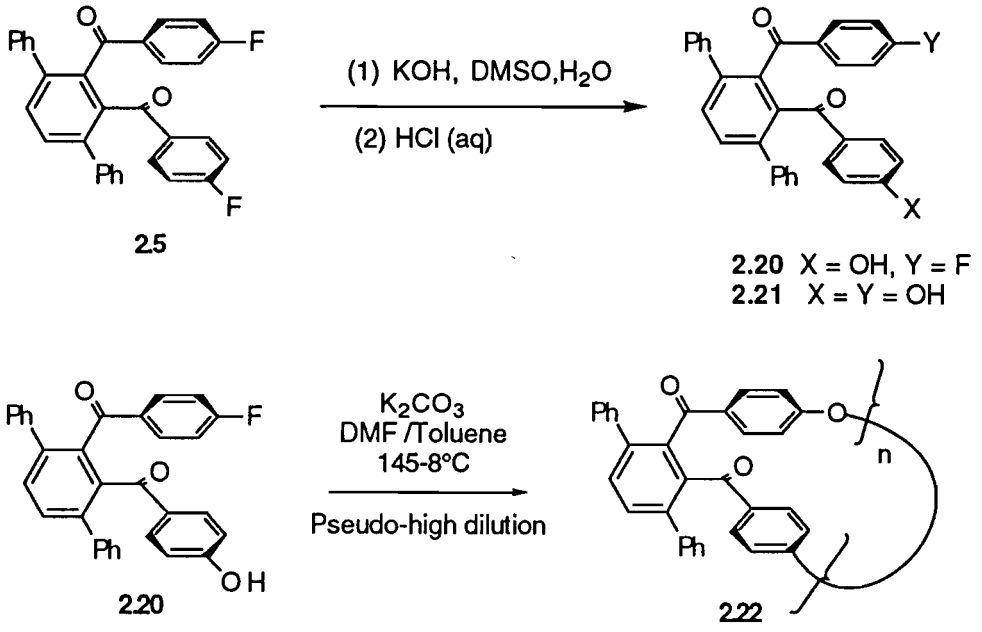


Figure 2.12. MALDI-TOF-MS spectrum of random co-cyclic **2.14.**



Synthesis of cyclic(aryl ether ketone) using an unsymmetrical AB type monomer. Cyclic oligomers **2.8**, **2.9**, and **2.10** were obtained by a AA+BB approach where two symmetrical monomers, difluoro monomers **2.4**, **2.5**, and **2.6** and bisphenols **2.7**, were condensed together to form the desired oligomers (Scheme 2.1). We have also studied the synthesis of cyclic(aryl ether ketone) by a different synthetic approach, in which an unsymmetrical AB type fluoro-hydroxy monomer **2.20** was used to prepared cyclic oligomer **2.22** (Scheme 2.2).

Scheme 2.2



2.5

2.20 X = OH, Y = F
2.21 X = Y = OH

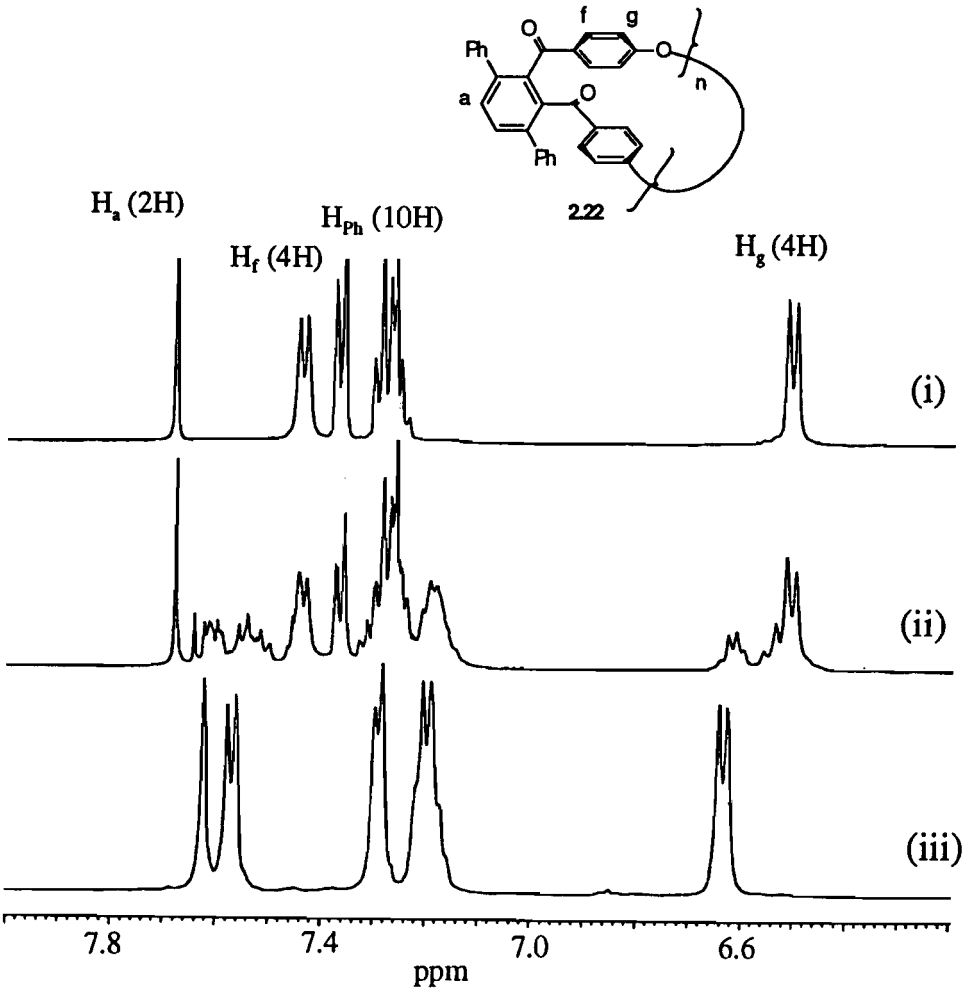
2.20

2.22

The fluoro-hydroxy monomer **2.20** was conveniently prepared by partial hydrolysis of the difluoro-monomer **2.5** with KOH in DMSO and water solution. (Scheme 2.2). In the hydrolysis reaction 1.5 equivalents of KOH were used; therefore, the reaction only consumed 50% of the starting materials, as indicated by HPLC. The reason for using less than stiochiometric amount of KOH is to suppress the formation of dihydroxy compound **2.21**, which is quite difficult to separate from the desired product **2.20**. We found that the use of 1.5 equivalents of KOH gives a good conversion (~50% conversion) of difluoro compound **2.5** to fluoro-hydroxyl compound **2.20** while keeping the yield of dihydroxy compound **2.21** less than 1%. Fluoro-hydroxy monomer **2.20** can then be easily separated from the starting material **2.5** by extracting the crude product with aqueous KOH solution.

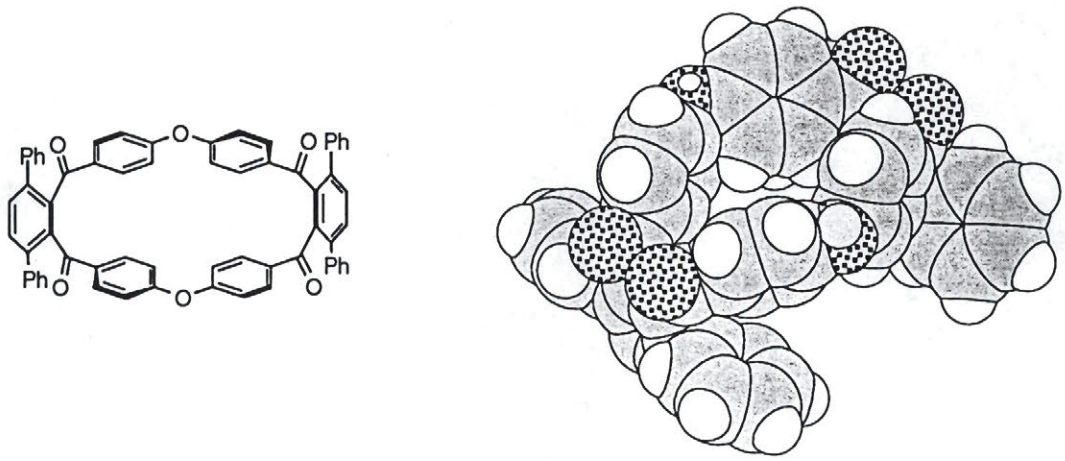
With the appropriate monomer at hand, we applied similar cyclization conditions. Cyclic oligomer **2.22** was obtained in 80 % isolated yield. It was interesting to find that 55 wt % of the material obtained is a 26 member cyclic dimer **2.22(n=2)**, based on MS, GPC and ^{1}H NMR (Figure 2.13) results. This procedure turned out to be an efficient synthesis of macrocycle **2.22(n=2)**, which may have potentially interesting molecular recognition and catalysis properties for high temperature and hostile environments. The dimer **2.22(n=2)** was less soluble in chloroform, while the rest of the cyclic oligomers are readily soluble, therefore it can be separated easily from the rest of the oligomers, and was characterized by spectroscopic methods.

Figure 2.13. ^{1}H NMR (500 MHz, $CDCl_3$) of (i) cyclic dimer **2.22(n=2)**, (ii) cyclic oligomer **2.22** & (iii) the corresponding high molecular weight linear polymer of **2.22**.



Examination of the molecular model of the dimer **2.22(n=2)** indicated that it is free of ring strain and has a very close distance between the ether oxygen atoms 7.4 Å (Figure 2.14).[14] The high yield of dimer may be the due to the fact that the 1,2-dibenzoylbenzene group can adopt a conformation in which the ends of the benzoyl arm can be brought very close together.

Figure 2.14. 3D model of dimer **2.22**(n=2).



2.2 Synthesis of cyclic phthalazine and isoquinoline oligomers

Cyclic phthalazine. Cyclic diketones **2.8b** and **2.8c** can be converted to the corresponding phthalazine using hydrazine hydrate and hydrochloric acid with dioxane as solvent.[15] Cyclic oligomers **2.8b** and **2.8c** are soluble in refluxing dioxane, the resulting products precipitate out of the reaction mixture and this facilitates the isolation of the phthalazine cyclic oligomer. (Scheme 2.3 & Table 2.8).

Scheme 2.3

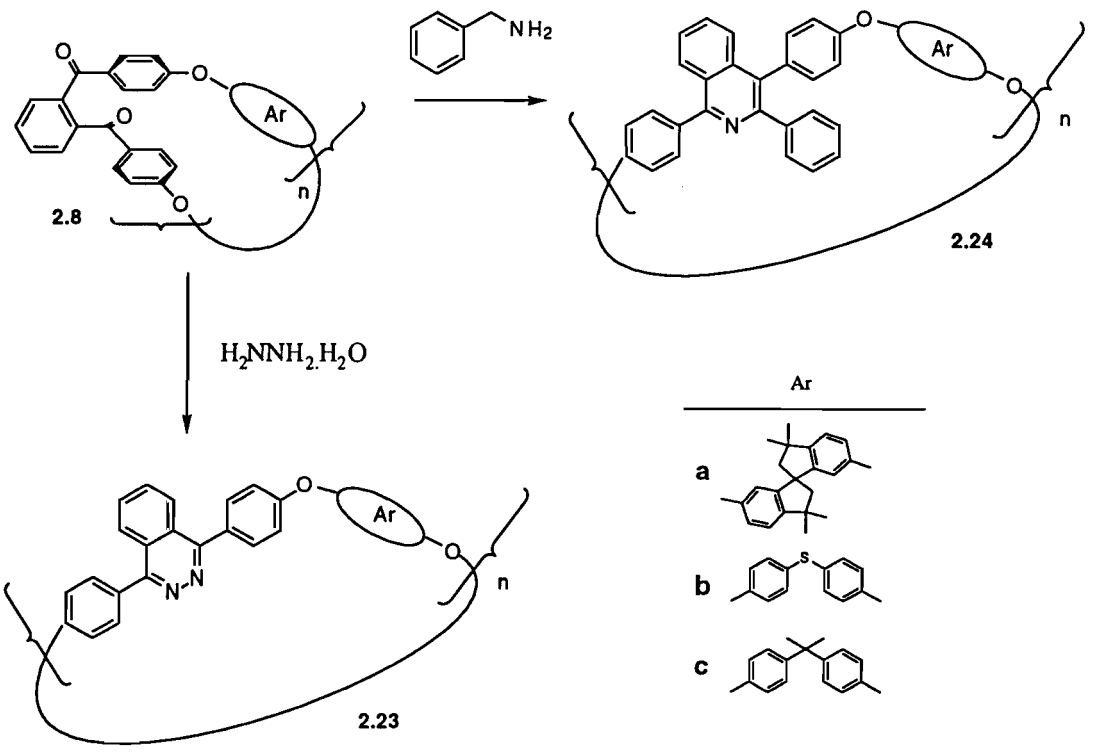


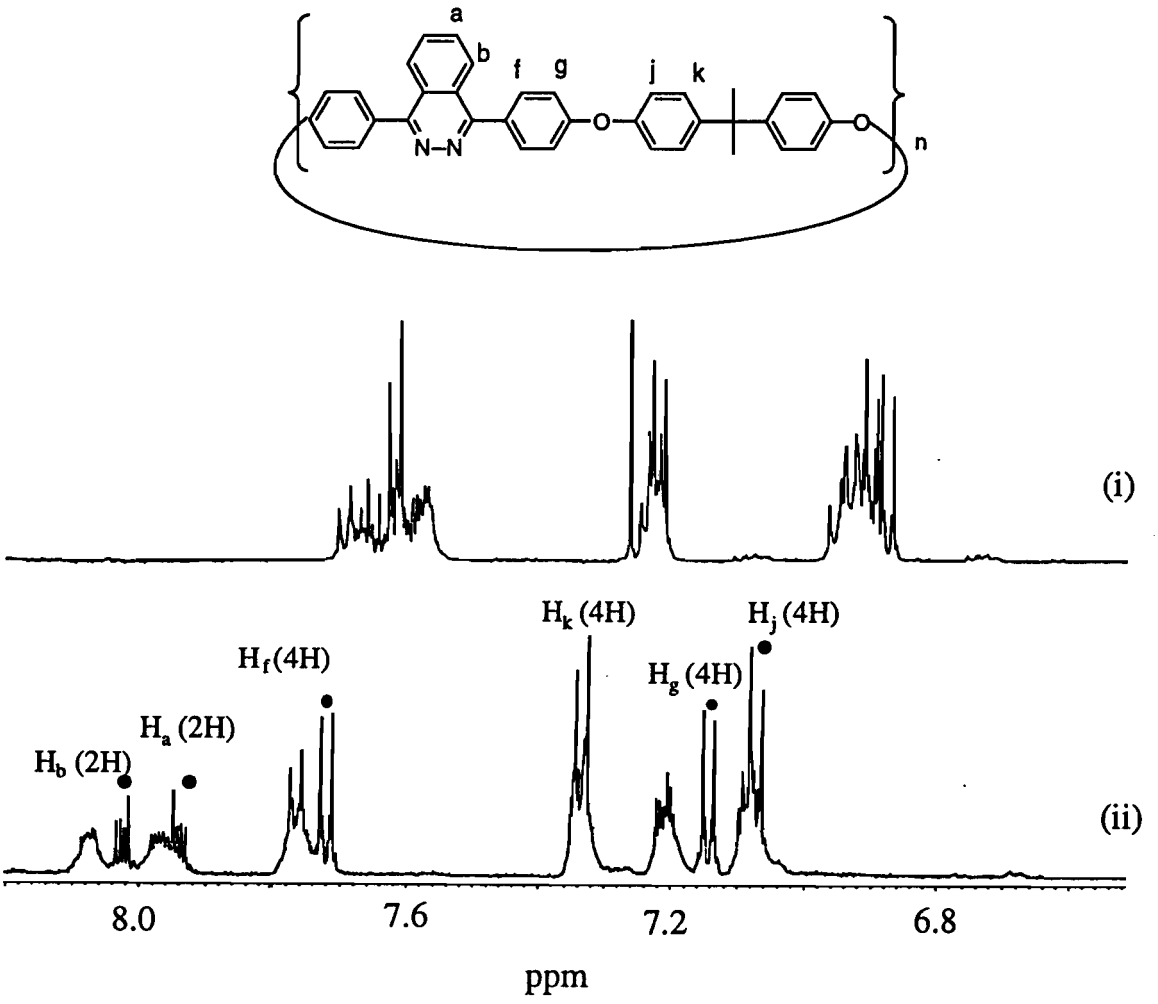
Table 2.8. Yields and thermoanalyses of cyclic phthalazine and isoquinoline oligomers.

Cyclic oligomer	Yield(%)[a]	Tg (°C) [b]	Tm (°C) [b]	TGA (°C) [c]
2.23a	90	230 (250)	n.d. [d]	420
2.23b	90	n.d.	n.d. [d]	480
2.23c	80	217(215)	n.d. [d]	450
2.24c	85	211(226)	n.d. [d]	530

[a] Isolated yield. [b] Measured on DSC under nitrogen atmosphere (50 mL/min), heating rate was 20°C/min, number in brackets is the Tg of the corresponding high molecular weight linear polymer. [c] Reported 5% weight loss under nitrogen atmosphere (200 mL/min), heating rate was 20°C/min. [d] n.d. = Not detected.

A ^{1}H NMR of cyclic phthalazine oligomer **2.23c** together with the cyclic ketone oligomer **2.8c** are shown in Figure 2.15. After transformation, proton signals of the dimer become well separated from the rest of the oligomers as indicated in Figure 2.15.

Figure 2.15. ^{1}H NMR (500 MHz) of (i) cyclic ketone oligomer **2.8c** in $CDCl_3$; (ii) cyclic phthalazine oligomer **2.23c** in DMSO-d_6.; • indicate the signals from the cyclic dimer (n=2) of **2.23c**.



In the case of the preparation of cyclic phthalazine **2.23a** from **2.8a**, the cyclic monomer of **2.8a** has to be removed first. The condensation of hydrazine with cyclic monomer of **2.8a** did not result in the desired cyclic phthalazine cyclic monomer of **23a(n=1)**, instead undesirable hydrazides **2.25** and **2.26** were obtained as shown in Scheme 2.4 according to FAB-MS analysis. Examination of a molecular model of the cyclic monomer of **2.23a(n=1)** (Figure 2.16) reveals that it is a highly strained

macrocycle. The two phenyl arms on the phthalazine moiety are forced to be bent inward. This may explain why cyclic monomer of **2.23a(n=1)** was not obtained.

Scheme 2.4

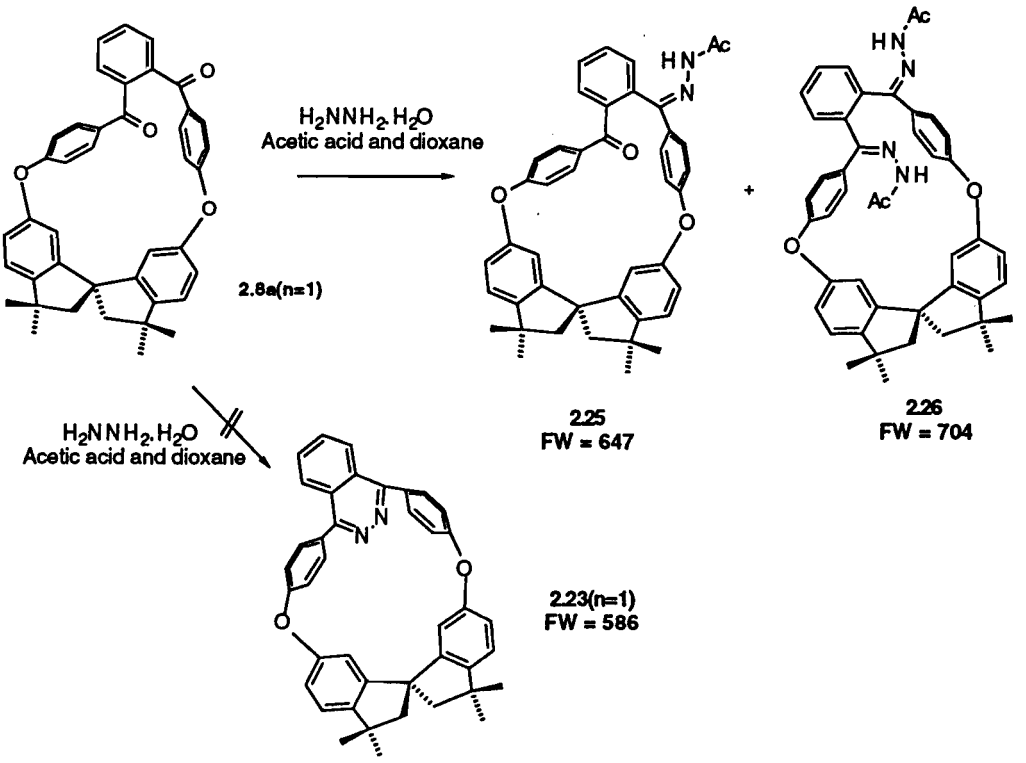
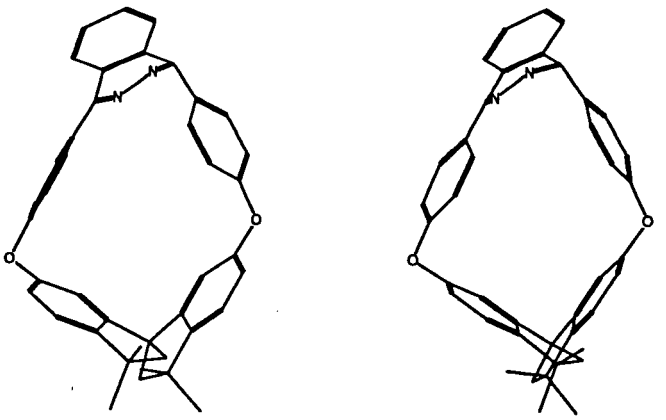


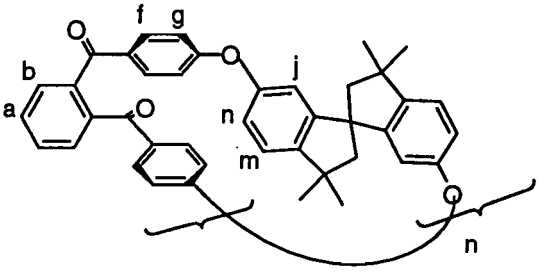
Figure 2.16. 3D models of cyclic monomer of 2.23a(n=1).

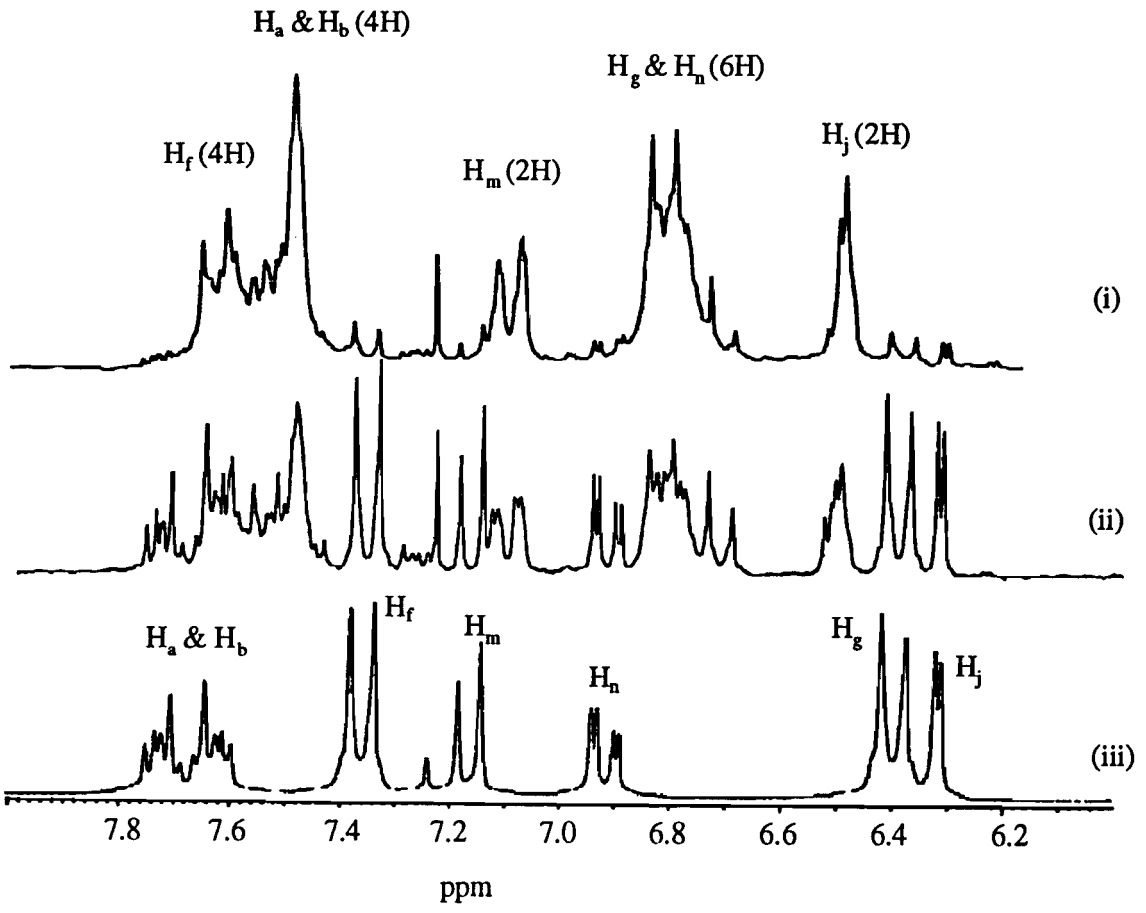


Removal of the cyclic monomer **2.8a(n=1)** from the rest of the oligomers **2.8a** can be achieved by selective precipitation, since **2.8a(n=1)** has lower solubility in chloroform.

^{1}H NMR clearly indicated that the cyclic monomer can be reduced down to ~3 wt%, as the proton signal of **2.8a(n=1)** are well separated from the other signals (Figure 2.17). The resulting cyclic phthalazine oligomers **2.23a** obtained were treated with acetic acid and sodium nitrite to covert the small amount of undesirable hydrazides **2.25** and **2.26** back to cyclic monomer **2.8a(n=1).** [16]

Figure 2.17. ^{1}H NMR (200 MHz, $CDCl_3$) of (i) cyclic oligomer **2.8a** with **2.8a(n=1)** depleted, (ii) cyclic oligomer **2.8a** as prepared, and (iii) cyclic monomer **2.8a(n=1).**





Cyclic isoquinolines. Treating the oligomer **2.8c** with benzylamine in the presence of the strong base 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) under reflux condition in chlorobenzene resulted in the cyclic isoquinoline oligomer **2.24c** in 30 h (Scheme 2.3 & Table 2.8).[17] A MALDI-TOF-MS spectrum of **2.24c** is shown in Figure 2.18. Signals up to n=7 were detected (Table 2.9). Both phthalazine and isoquinoline oligomers are very insoluble in chloroform and DMSO. The Tgs are not apparent in the DSC trace, and we believe that the materials are highly crystalline and have Tms beyond the decomposition temperatures.

Figure 2.18. MALDI-TOF-MS spectrum of cyclic isoquinoline **2.24c.**

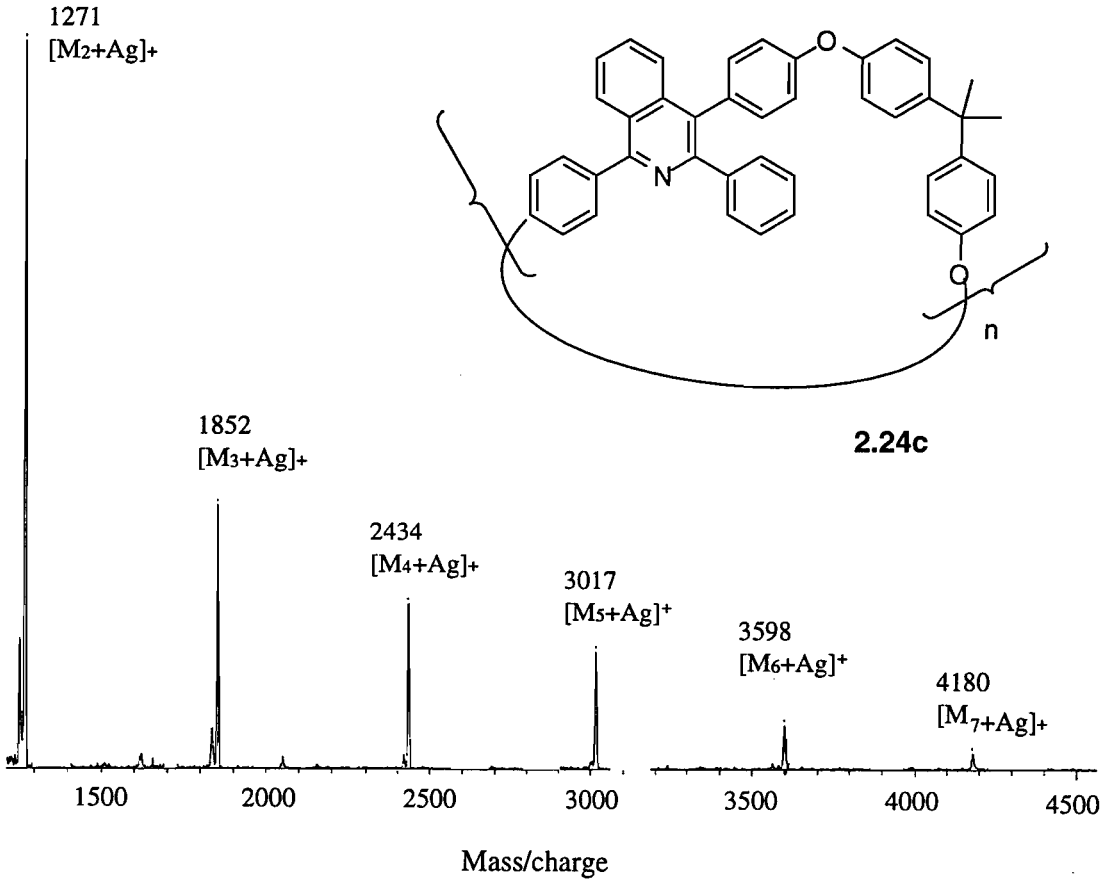


Table 2.9. MALDI-TOF-MS data of cyclic oligomer **2.24c** using dithranol as matrix and $AgCF_3CO_2$ as cationization agent.

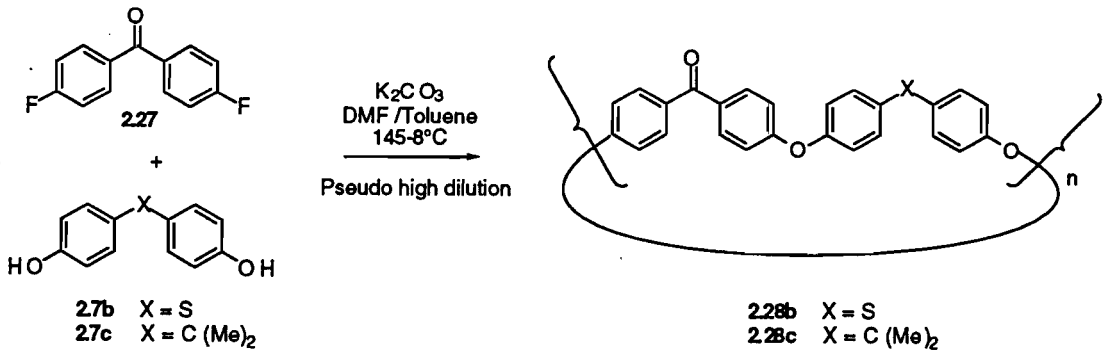
Signal(m/e)	Rel. Intensity(%)	Assignment[a]	Calculated m/e	Deviation (Da)[b]
1271	100	M_2+Ag	1271	0
1852	30	M_3+Ag	1853	- 1
2434	17	M_4+Ag	2435	- 1
3017	12	M_5+Ag	3016	+ 1
3598	4	M_6+Ag	3598	0
4180	1	M_7+Ag	4180	0

[a] M_x represent the molecular ion with x repeating units, average molecular weight calculated for repeating unit $C_{42}H_{31}NO_2$ = 581.7, [b] deviation = experimental value - calculated value.

2.3 Cyclic(aryl ether ketone)s from aromatic difluorides with different geometrical constrains

Cyclic(aryl ether ketone)s from difluorobenzophenone 2.27. In order to further explore the synthetic utility of our cyclization procedure, we employed difluorobenzophenone **2.27** for the preparation of cyclic aryl ether ketone. It was found that difluorobenzophenone **2.27** condensed readily with bisphenols to give high yields of cyclic oligomers **2.28b & c** with our cyclization conditions (Scheme 2.5 & Table 2.10). GPC of oligomer **2.28c** has a typical distribution similar to that of the 1,2-dibenzoylbenzene containing cyclic oligomer **2.8** (Table 2.11 & Figure 2.19). On the other hand, the GPC of cyclic oligomer **2.28b** indicated that only very low molecular weight oligomers were formed, oligomers with *DP* > 7 were not observed (Table 2.11 & Figure 2.19).

Scheme 2.5



2.7b X = S
2.7c X = C (Me)$_2$

2.28b X = S
2.28c X = C (Me)$_2$

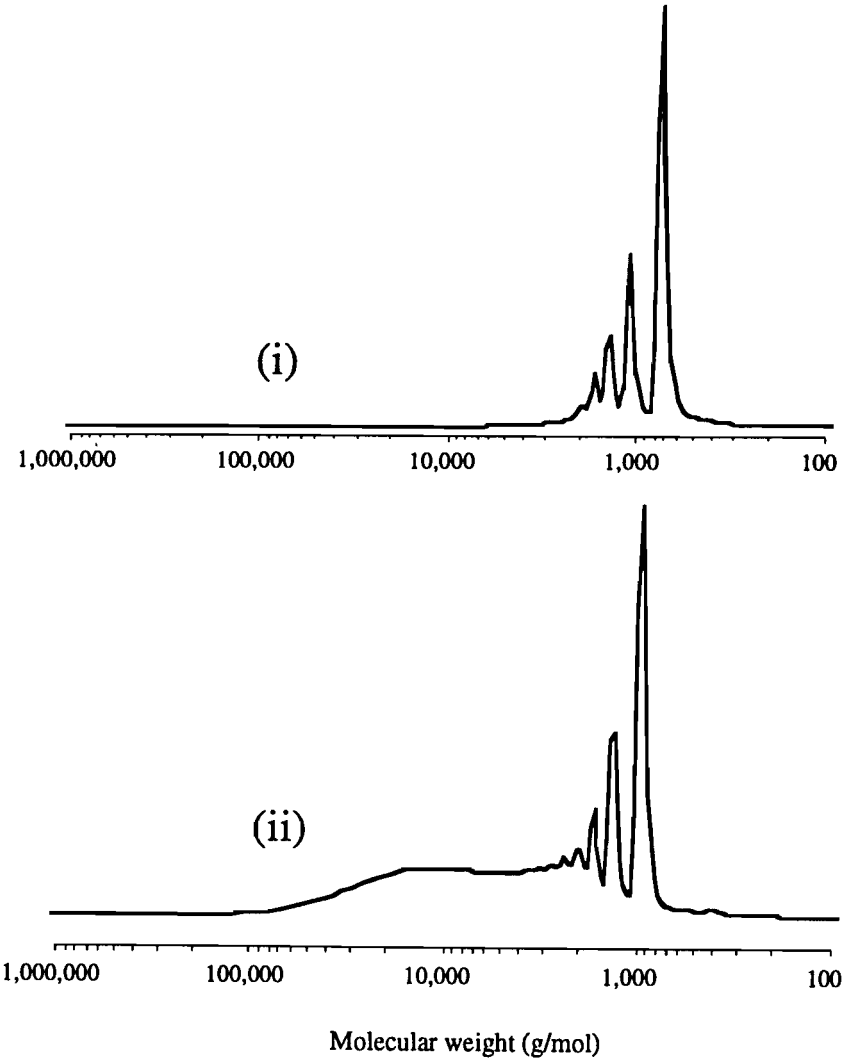
Table 2.10. Yields and thermoanalyses of cyclic oligomer **2.28b**, **2.28c**, and **2.30b**.

Cyclics	M_w(kg/mol)	M_n(kg/mol)	Tg (°C)	TGA(°C)	Tm(°C)	Yield(%)
2.28b	0.9	0.8	130	496	274/364	80
2.28c	5.9	1.3	160	500	355	88
2.30b	12.6	2.2	141	486	284	78

Table 2.11. Cyclic oligomers distribution (Wt %).

n	**2.28b**	**2.28c**	**2.30b**
2	56	39	17
3	23	15	10
4	12	8	7
5	6	5	6
>5	1	33	60

Figure 2.19. GPC traces of cyclic oligomers (i) **2.28b**, and (ii) **2.28c**.



The cyclic nature of the benzophenone containing cyclic oligomers **2.28b** & **2.28c** were further supported by the MALDI-TOF-MS spectra, which gave the desired signals of dimer to hexamer (Figure 2.20 & Table 2.12).

Figure 2.20. MALDI-TOF-MS spectrum of cyclic oligomer **2.28b.**

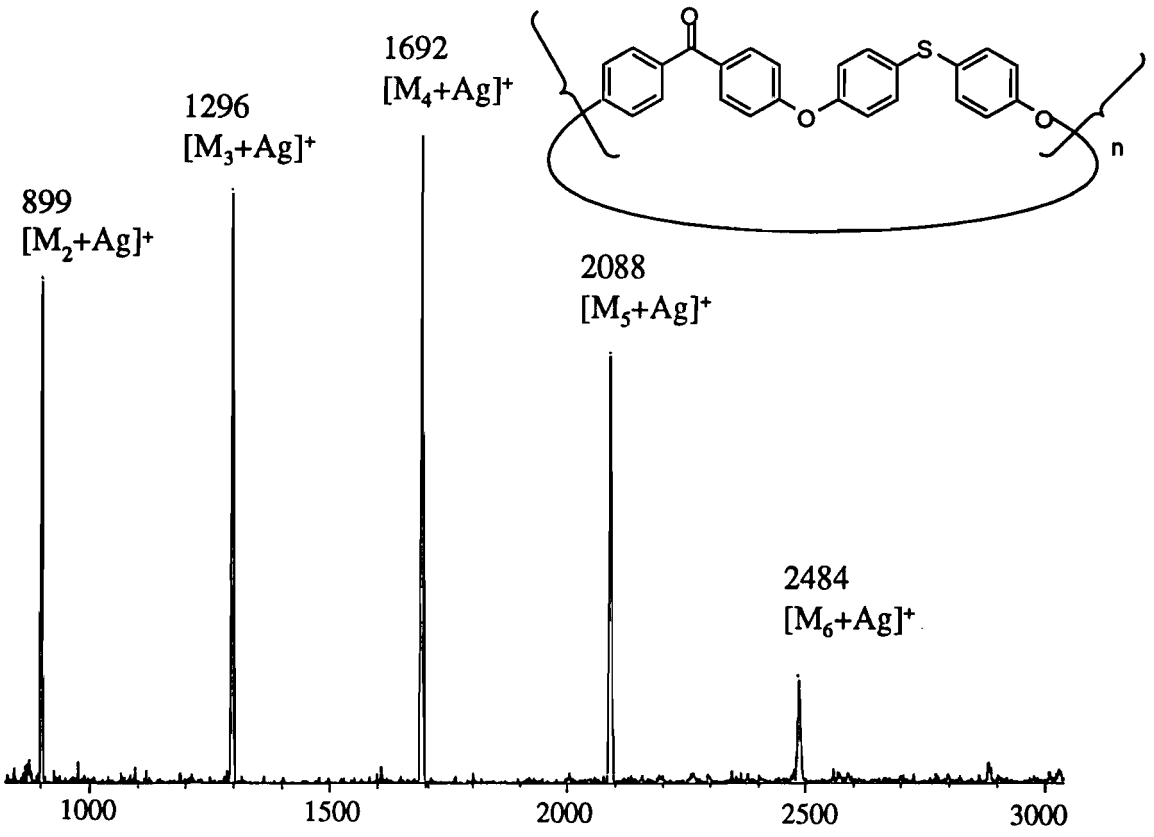


Table 2.12. MALDI-TOF-MS data of cyclic oligomer **2.28b** using dithranol as matrix and $AgCF_3CO_2$ as cationization agent.

Signal(m/e)	Rel. Intensity(%)	Assignment [a]	Calculated m/e	Deviation (Da)[b]
899	80	M_2+Ag	901	- 2
1296	100	M_3+Ag	1297	- 2
1692	99	M_4+Ag	1694	- 2
2088	70	M_5+Ag	2090	- 2
2484	15	M_6+Ag	2486	- 2

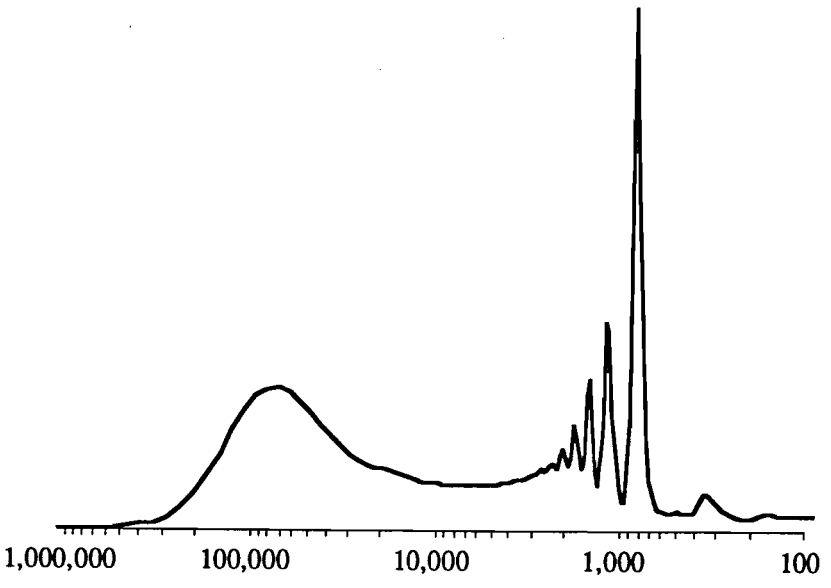
[a] M_x represent the molecular ion with x repeating units, average molecular weight calculated for repeating unit $C_{25}H_{16}O_3S$ = 396.5, [b] deviation = experimental value - calculated value.

Fukuyama has reported the synthesis of cyclic oligomer **2.28c** in his US patent. [18] He employed a synthetic method to similar ours, except that DMSO was used instead of DMF as solvent. He reported a shorter total reaction time, and higher final reactants concentration compared to our synthetic conditions (Table 2.13). We have repeated his experiment and found that the yield of cyclic oligomer **2.28c** was low compared to our method, in which ~50 wt % of the product consisted of high molecular weight polymer as indicated by GPC analysis (Figure 2.21).

Table 2.13. Comparison of cyclization conditions for cyclic oligomer **2.28c**.

	Fukuyama's	Present work
Addition time (h)	3	8
Total reaction time (h)	8	16
Final reactants conc (mM)	80	40
M_n (kg/mol)	2.5	1.3
M_w (kg/mol)	32	6

Figure 2.21. GPC trace of cyclic oligomer **2.28c** obtained using the procedure of Fukuyama.



Cyclic(aryl ether ketone) from 1,3-bis(4-fluorobenzoyl)benzene 2.29. We have attempted to prepare cyclic (aryl ether ketone) **2.30b** from 1,3-bis(4-fluorobenzoyl)benzene **2.29** (an isomeric analogue of difluoro-monomer **2.4**) and bisphenol **2.7b** (Scheme 2.6). However, 1,3-bis(4-fluorobenzoyl)benzene **2.29** is not readily soluble in DMAc or DMF; therefore, a batch process instead of pseudo-high-dilution conditions was employed. MALDI-TOF-MS (Figure 2.22 & Table 2.14) analysis indicated that this procedure yields cyclic oligomers; however, the yield is low as indicated by the GPC, where considerable amount of high molecular weight material is also obtained (Figure 2.23 & Table 2.11).

Scheme 2.6

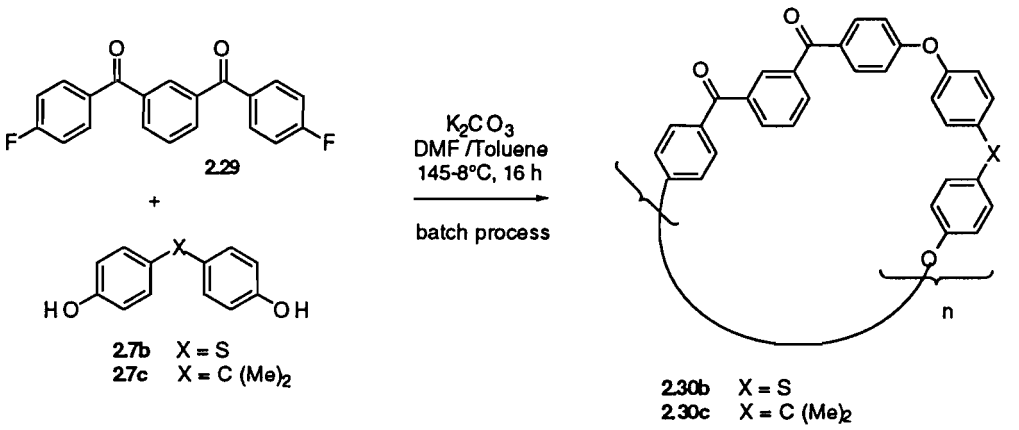


Table 2.14. MALDI-TOF-MS data of cyclic oligomer **2.30b** using dithranol as matrix and $AgCF_3CO_2$ as cationization agent.

Signal(m/e)	Rel. Intensity(%)	Assignment [a]	Calculated m/e	Deviation (Da)[b]
1109	100	M_2+Ag	1109	0
1610	41	M_3+Ag	1610	0
2112	30	M_4+Ag	2110	+2
2612	27	M_5+Ag	2611	+1
3113	20	M_6+Ag	3111	+2
3612	12	M_7+Ag	3612	0
4113	8	M_8+Ag	4112	+1

[a] M_x represent the molecular ion with x repeating units, average molecular weight calculated for repeating unit $C_{32}H_{20}O_4S$ = 500.6 [b] deviation = experimental value - calculated value.

Figure 2.22. MALDI-TOF-MS spectrum of cyclic oligomer **2.30b.**

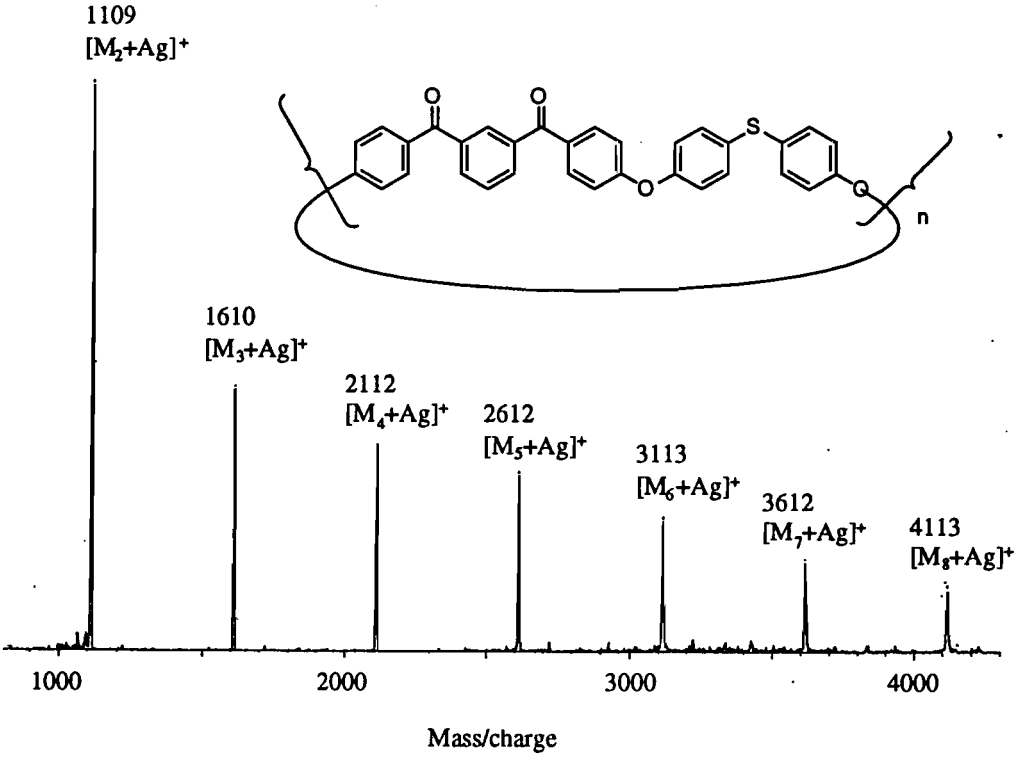
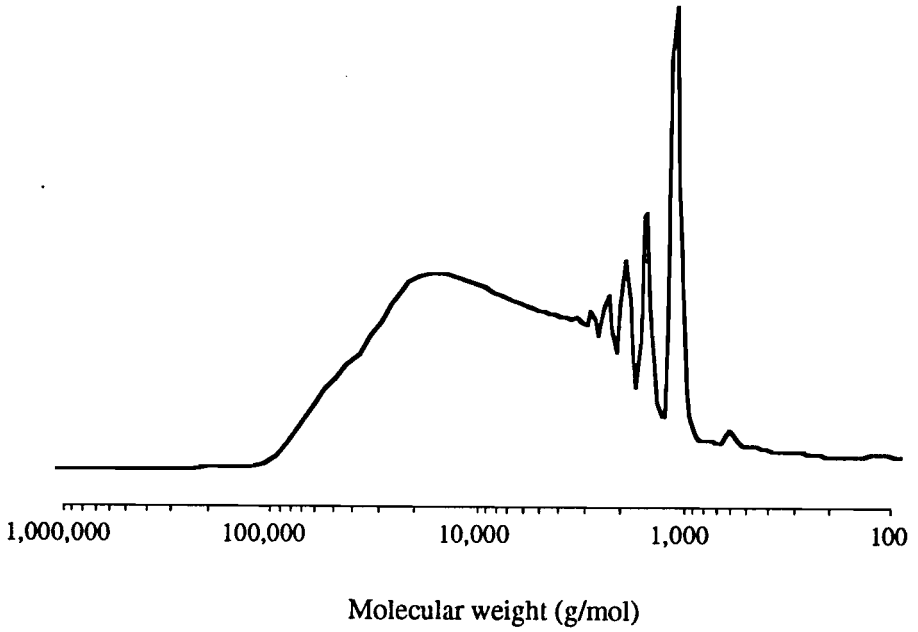


Figure 2.23. GPC trace of cyclic oligomer **2.30b.**



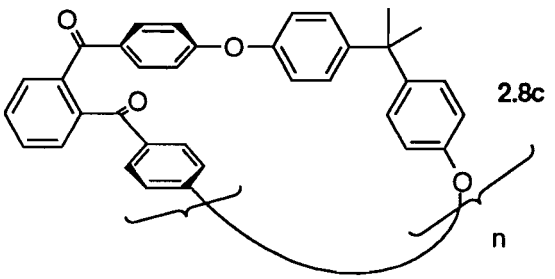
Mullins et al have reported the preparation of cyclic oligomer **2.30c** from difluoro monomer **2.29** with BPA **2.7c** in their US patent. [19] In their procedure, they condensed difluoro-monomer **2.29** with BPA **2.7c** to give cyclic oligomer **2.30c** in 60% yield. They employed NaOH as base and DMSO as solvent. They have employed the pseudo-high dilution method by preparing a dilute solution of **2.29** (125 mM). The reactants were delivered into the reaction vessel over a period of 6 hr, and the reaction mixture was refluxed for another 18h. The final concentration of reactants was 10 mM when the addition was completed (Table 2.15). It is obvious that the monomer **2.29** is not readily soluble in DMSO; therefore, they had to prepare a dilute (125 mM) solution of **2.29** in order to employ the pseudo-high dilution conditions. Furthermore, their final reactant concentration was 4 times lower that our reported method, hence they were able to isolate the monocyclic (*DP*=1) from the reaction mixture; however, they didn't specify the yield of the monocyclic materials.

Table 2.15. Comparison of cyclization conditions for cyclic oligomer **2.30**.

	Mullins's	Present work
Addition time (h)	6	0
Total reaction time (h)	24	16
Final reactant conc. (mM)	10	40

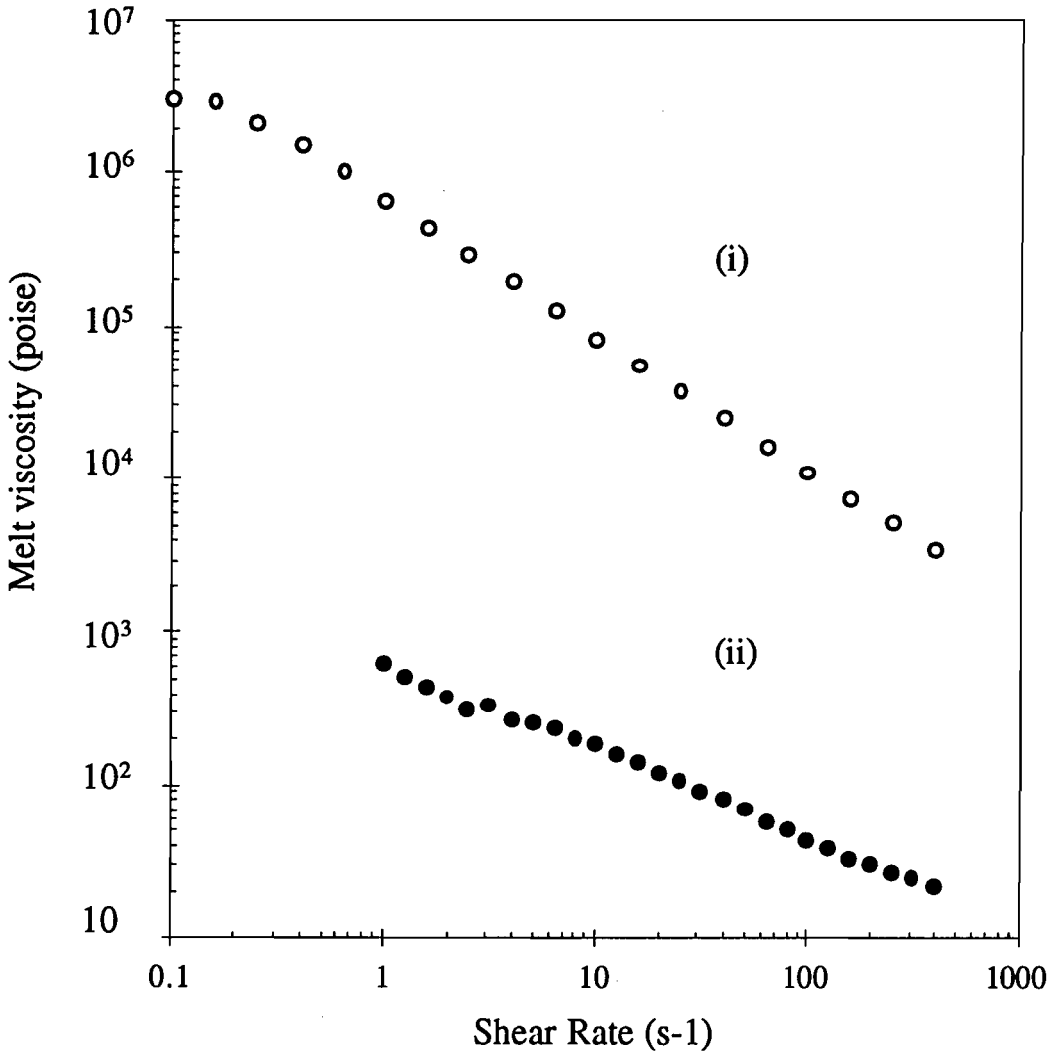
2.4 Preliminary rheology study on cyclic(aryl ether)s

As it has been mentioned earlier the low melt viscosity of the cyclic oligomers is the key feature for their potential application as resins for advanced composites and adhesives. Therefore, the melt viscosity of some of the cyclic oligomers prepared have been measured using a rotational rheometer.[20] For example, the melt viscosity measurements of the cyclic oligomer **2.8c** and its corresponding high molecular weight polymer at 300 °C are shown in Figure 2.24 . It is obvious that the melt viscosity of the cyclic oligomer **2.8c** is indeed orders of magnitude lower than its corresponding high molecular weight polymer, as expected.



2.8c

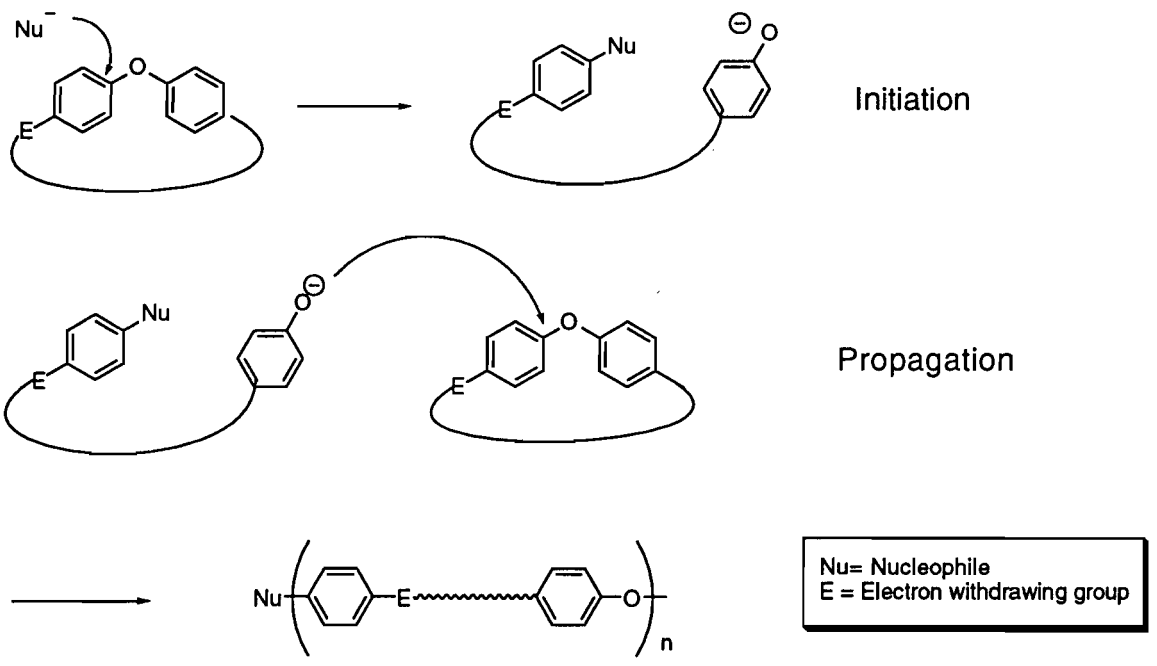
Figure 2.24. Melt viscosity measurement of (i) corresponding linear polymer of **2.8c** (M_w = 100 kg/mol), (ii) cyclic oligomer **2.8c** at various shear rates.



2.5 Preliminary study on the ring opening polymerization of cyclic(aryl ether)s

Polymerization using anionic catalyst. Ring opening polymerization (ROP) of the cyclic(aryl ether ketone) oligomers prepared can be initiated through an ether exchange reaction (Scheme 2.7). Since the aryl ether linkage is activated by an electron-withdrawing carbonyl group, it will undergo ether exchange reaction readily in the presence of a nucleophilic catalyst.[21,22]

Scheme 2.7



Therefore, melt polymerization has been performed on the cyclic oligomers **2.8b** and **2.8c** with 1 mole percent of CsF as catalyst. Both oligomers undergo facile polymerization within 30 min at 300°C and 340°C respectively to give high molecular weight polymers. Cyclic oligomer **2.8b** gave polymer with M_w = 510 kg/mol and M_n = 18 kg/mol and **2.8c** gave polymer with Mw =165 kg/mol and M_n = 10 kg/mol. A GPC trace for the polymer from **2.8c** is shown in Figure 2.25.

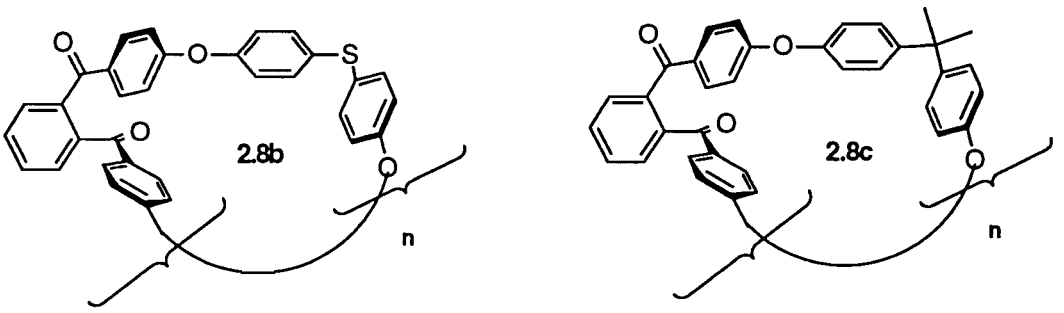
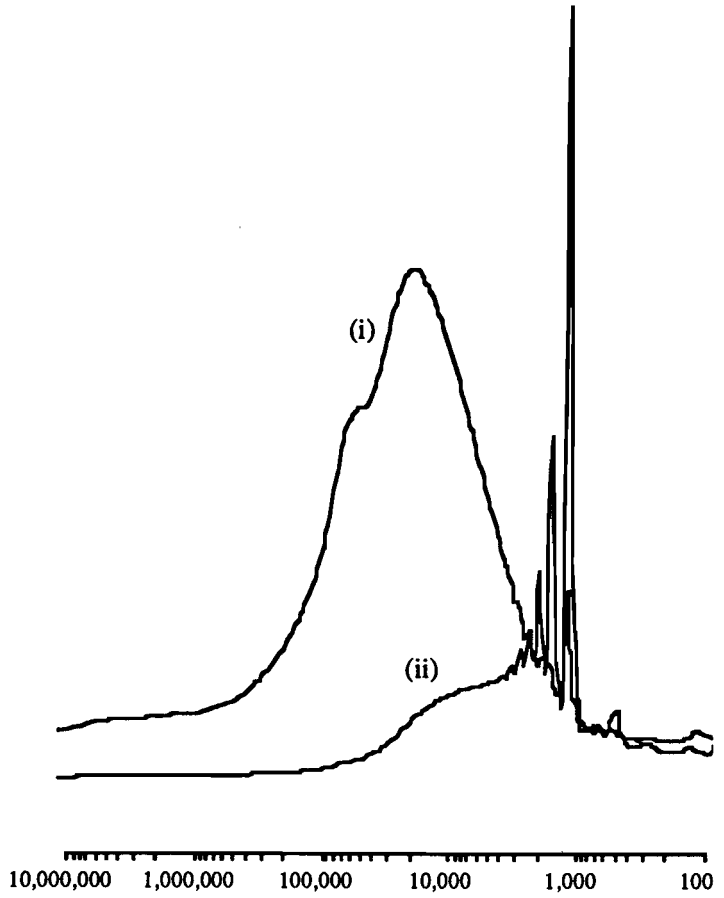


Figure 2.25. GPC traces of (i) polymerization product of cyclic oligomer **2.8c**, (ii) cyclic oligomer **2.8c**.



We find that polymerization using CsF results in polymer with broad molecular weight distribution containing an extremely high molecular weight fraction, up to a million, based on GPC analysis. When polymerization was performed at higher temperature and longer time, the polymer became extremely high weight average molecular weight (M_W), and became insoluble in chloroform. We suspected the large molecular weight distribution may result from a branching side reaction, which gave rise to some extremely high molecular weight fraction. Furthermore, the broad distribution can also be attributed to the presence of an equilibrium amount of cyclic oligomers as a result of the ring-chain equilibrium nature of ROP.

Cyclic oligomers **2.8b** and **2.8c** mixed with 1 mole % of CsF have been compression molded at moderate temperatures and *in situ* polymerized into rectangular bars. Preliminary dynamical mechanical thermal analysis (DMTA) results (Figure 2.26) show that the stiffness of both materials is maintained up to their Tgs. The polymer **2.8b**

shows a much sharper glass transition and higher value of mechanical damping, which indicates this polymer should have much higher toughness.

Figure 2.26a. DMTA spectrum of polymer from cyclic oligomer **2.8b.** Storage moduli (E'), loss moduli (E") and loss tangents (tanδ) were obtained as a function of temperature at a heating rate of 2°C/min.

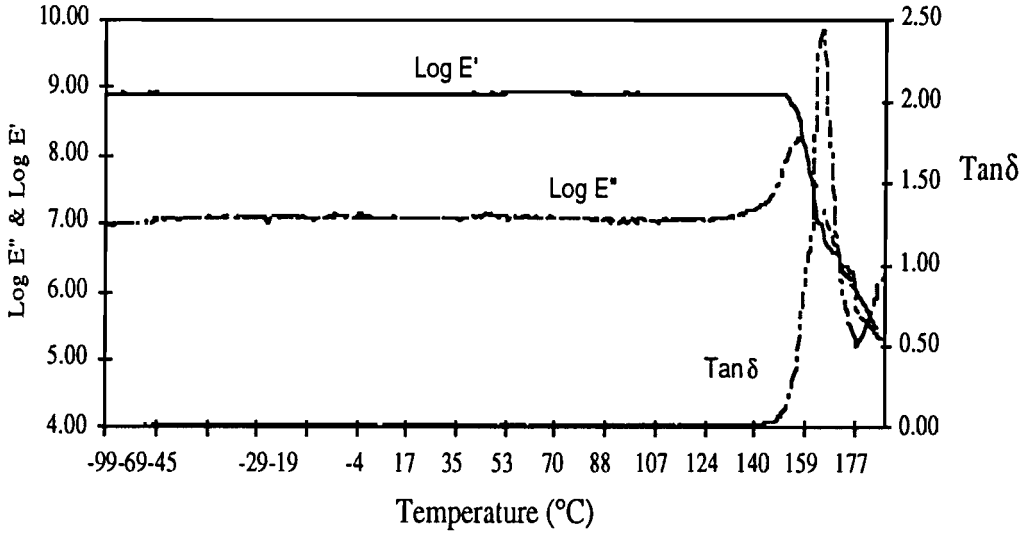
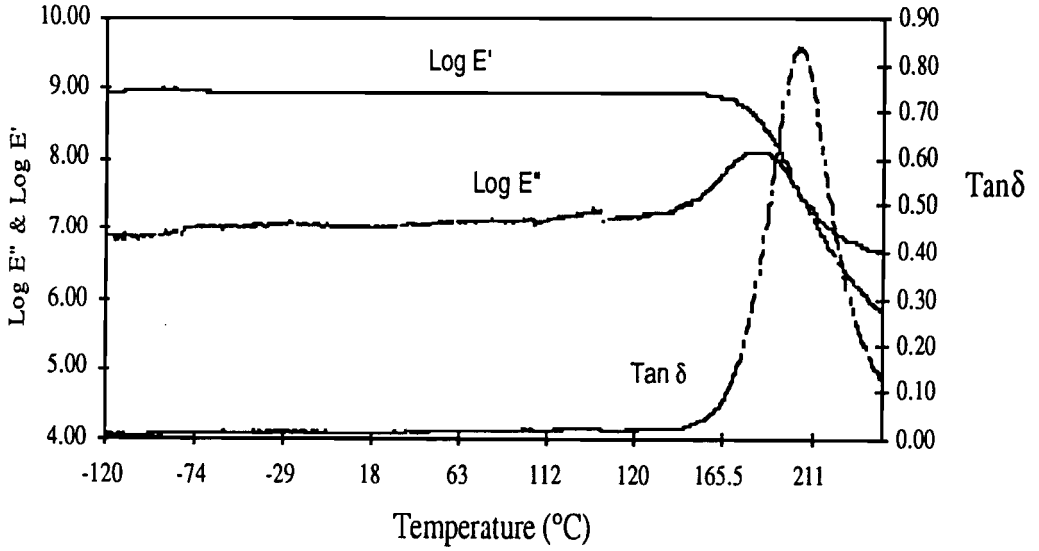
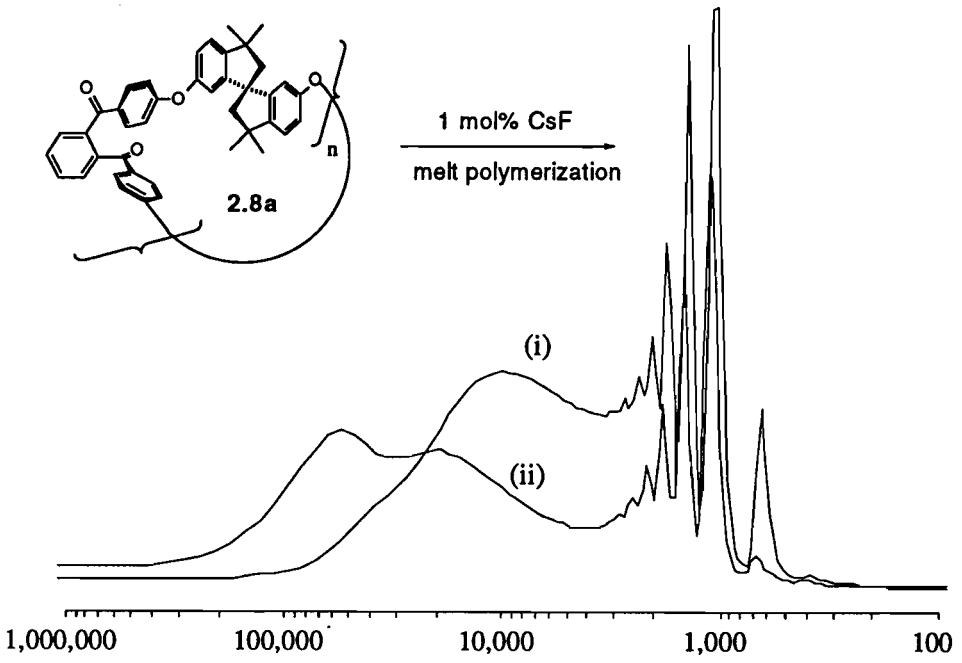


Figure 2.26b. DMTA spectrum of polymer from cyclic oligomer **2.8c.**



On the other hand, polymerization of SBI containing cyclic oligomer **2.8a** was found to be sluggish. GPC analysis of the resulting materials indicated that a large amount of cyclic oligomers remained after the polymerization even at very high polymerization temperature (400 °C) (Figure 2.27). It suggests that in the ring opening polymerization of cyclic oligomer **2.8a,** the equilibrium position of the ring-chain equilibrium lies on the side of the cyclic oligomers due to the special configuration of SBI. Brunelle has reported that cyclic carbonate prepared from SBI does not undergo polymerization readily, even though using SBI has the advantage of promoting the formation of cyclic oligomers.[23]

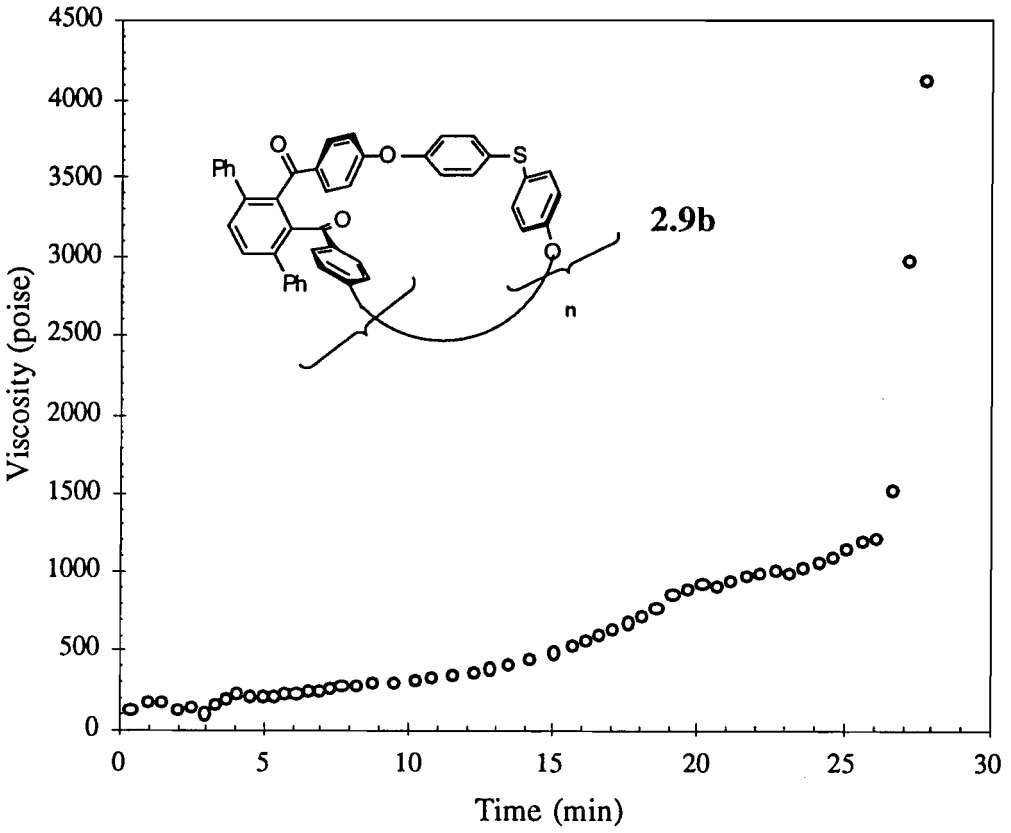
Figure 2.27. GPC traces of the of polymers obtained from melt polymerization of cyclic oligomer **2.8a** at (i) 340 °C for 30 min, (ii) 400 °C for 30 min.



Ring opening polymerization through a radical mechanism. It was interesting to find that cyclic oligomers containing a thio-ether linkage such as **2.8b**, and **2.9b** underwent polymerization without catalyst. We are aware that it might be possible that trace amounts of residual potassium salt can induce polymerization at elevated temperature through an anionic mechanism.[24] Therefore, cyclic oligomer **2.9b** has been carefully purified to remove all the residual potassium salts by precipitation into 0.2N hydrochloric acid. Atomic absorption analysis indicated that the residual potassium ion is less that 5 ppm.

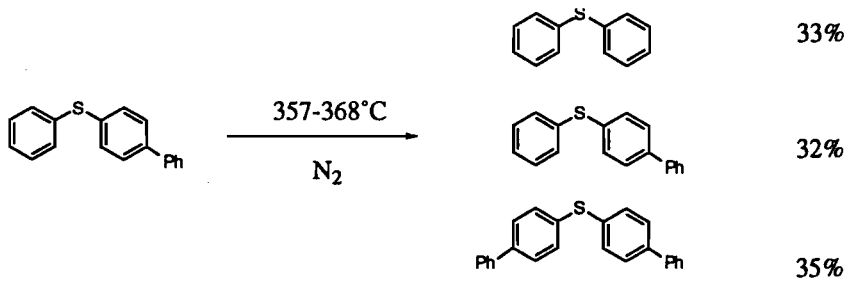
A rheology study of purified cyclic oligomer **2.9b** at 390 °C clearly shows that there is a molecular weight built up as indicated by sharp jump in viscosity (Figure 2.28). GPC analysis on the material after the rheology study indicated that the cyclic oligomer was transformed into high molecular weight polymer (M_w = 600 kg/mol, M_n = 25 kg/mole).

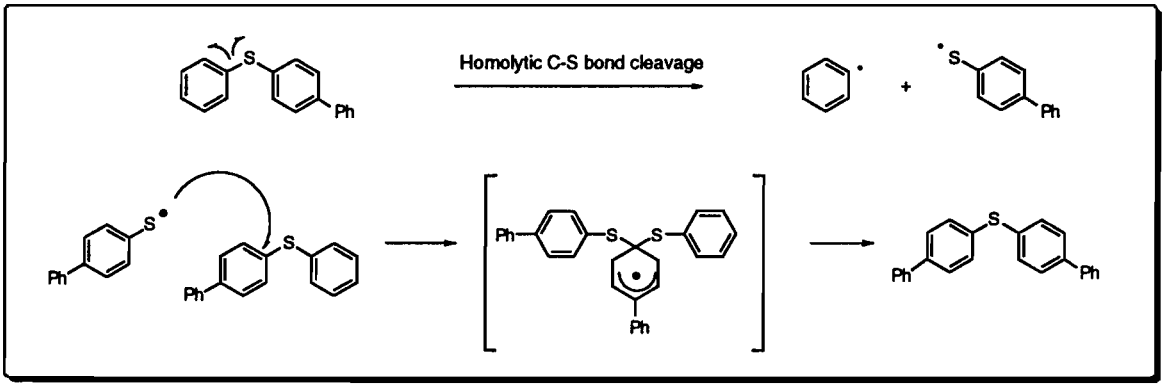
Figure 2.28. Melt viscosity measurement of cyclic oligomer **2.9b** at 390 °C under a shear rate of 10 S^{-1}.



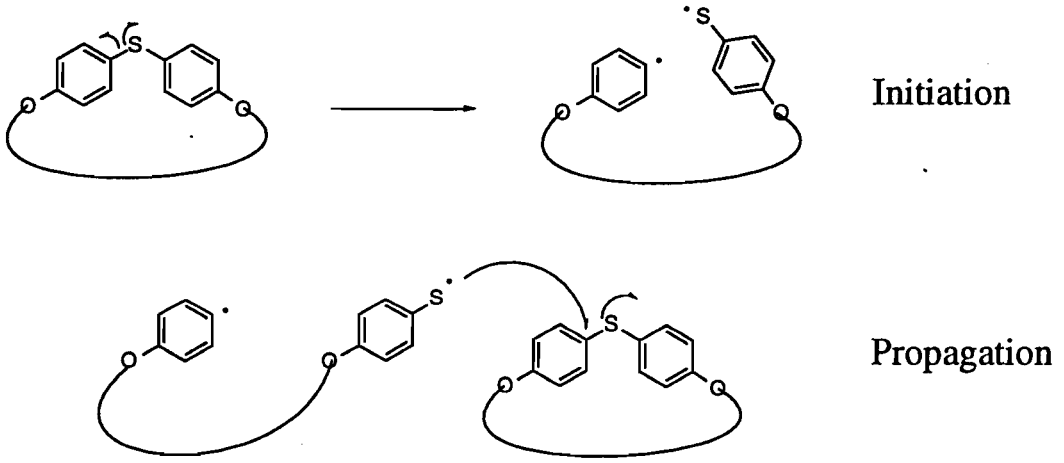
It has been reported that diaryl sulfides underwent a redistribution reaction at elevated temperature. It was suggested that the redistribution is initiated through homolytic C-S bond cleavage to give aryl and sulfide radicals followed by a radical aromatic substitution reaction as shown in Scheme 2.8. [25] Hence, one probable explanation for the thermal polymerization of thio-ether containing cyclic oligomer **2.9b** would be that the sulfur-carbon bond undergoes thermal homolytic cleavage and initiates a free radical polymerization of the sulfur containing cyclic oligomers as shown in Scheme 2.9.

Scheme 2.8



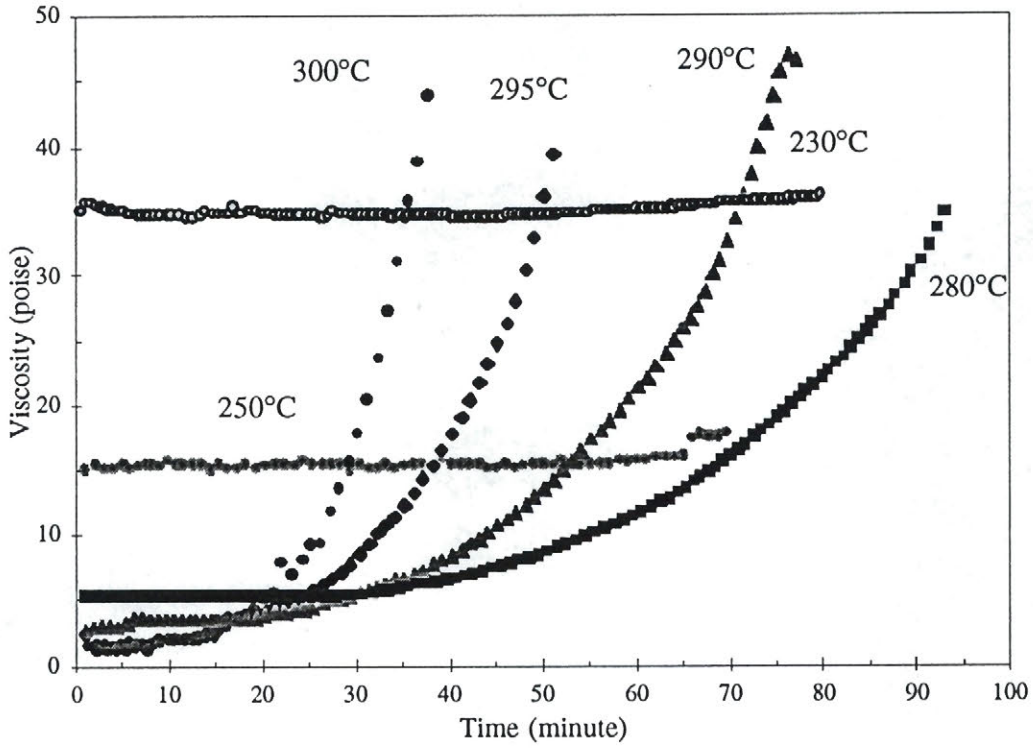


Scheme 2.9



Similar rheology studies have been carried on cyclic oligomer **2.8b** at various temperature (Figure 2.29). It was found that the cyclic oligomer is thermally stable up to ~250 °C. When the cyclic oligomer was heated above 280 °C, molecular weight build up was observed as indicated by the increase in viscosity. The higher the temperature the faster the molecular weight increase.

Figure 2.29. Melt viscosity measurement of cyclic oligomer **2.8b** at a shear rate of 100 S^{-1} at various temperature.



The discovery of the thermally induced ring opening polymerization of thio-ether containing cyclic(aryl ether)s oligomers provides a new direction, and advantages in design and polymerization cyclic(aryl ether) oligomers. For example, the use of metallic salts can be avoided, as the presence of trace amount of metallic salt can deteriorate the ultimate thermal stability of the polymer considerably. Furthermore, one may able to control the polymerization through the use of free radical initiators or inhibitors.

2.6 Conclusions

A high yield synthesis of cyclic(aryl ether ketone) oligomers containing a 1, 2-dibenzoylbenzene moiety via the nucleophilic aromatic substitution route has been developed. Chemical transformation of the 1,2-dibenzoylbenzene moiety of these cyclic(aryl ether ketone)s led to the preparation of novel cyclic(aryl ether phthalazine)s and cyclic(aryl ether isoquinoline)s. Matrix assisted laser desorption ionization - time of flight - mass spectrometry, which enables the detection of oligomers with mass up to 5000 Da, was shown to be a very powerful tool for the analysis and proof of the cyclic nature of the oligomers.

A preliminary rheology study on selected cyclic(aryl ether ketone)s showed that the viscosity of the cyclic oligomers is orders of magnitude lower than the high molecular weight polymers. Preliminary study on the melt polymerization of selected cyclic oligomers showed that these material undergo ring opening polymerization readily in the presence of anionic catalysts such as cesium fluoride to give high molecular weight polymers. It was discovered that thio-ether containing cyclic(aryl ether)s can undergo ring opening polymerization at temperatures above 350 °C without the use of catalyst, presumably the polymerization is initiated through a free radical mechanism.

2.7 Experimental

Instrumentation. ^{1}H, ^{13}C, and ^{19}F NMR experiments were performed at room temperature on Varian XL-200, XL-300 and Unity-500 NMR spectrometers. EI mass spectra were record on a Du Pont 21-492B spectrometer. Positive ion fast atom bombardment (FAB) mass spectra were record on a ZAB 2F HS spectrometer using 3-nitrobenzyl alcohol as matrix. MALDI spectra were performed on a Kratos Kompact MALDI-III TOF instrument with a maximum laser output of 6 mV at a wavelength of 337 nm. The ions produced from each laser shot were accelerated to 20 KeV into a 1 m drift region. The MALDI spectra were recorded at positive linear or reflectron mode. Sample concentrations were approximately 10-50 nmol/μL and 2,5-dihydroxybenzoic acid or dithranol were used as a matrix and $AgCF_3CO_2$ as cationization agent. Equal volumes were mixed and 0.6 μL placed on the target slide and air dried.

HPLC analyses were performed on a Du Pont Model 410 pump, ISS-100 autoinjector, and LC-235 diode array detector. THF/water gradient was used for the elution of product on C-8 reverse-phase column (4.6 x 256 mm). The gradient program was; step 1, 60 - 84 % THF over 17 min at exponent -2; step 2, 84 -100% THF over 1 min at exponent 1; step 3, 100% THF for 6 min; step 4, 100-60% THF over 2 min (recycle). GPC analyses were performed on a Waters 510 HPLC equipped with phenogel 5μ columns (7.8 x 300 mm), one linear, and three 500Å arranged in series and using chloroform as eluent, and a UV detector (254 nm). Thermoanalyses were obtained on Seiko 220 DSC and 220 TGA/DTA instruments.

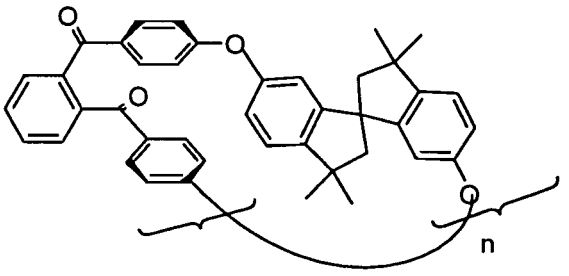
Dynamical mechanical property measurements were performed on a Polymer Laboratories dynamical mechanical thermal analyzer (DMTA) in the dual cantilever bending mode at a frequency of 1 Hz under nitrogen atmosphere. Storage moduli (E'), loss moduli (E") and loss tangents (tanδ) were obtained as a function of temperature at a heating rate of 2°C/min.

X-ray crystallography on cyclic dimer **2.8b(n=2)** was performed by Dr. A. M. Lebuis of Department of Chemistry, McGill University.

Rheology measurements of cyclic oligomers **2.8b**, **2.8c**, and **2.9b** were performed by Dr.Yi-Feng Wang of Department of Chemistry, McGill University. Compression molding and *in situ* polymerization of cyclic oligomers **2.8b**, and **2.8c** and DMTA measurement of resulting polymers were also performed by Dr.Yi-Feng Wang.

Starting materials. Difluoro-monomers **2.4**, **2.5**, and **2.6** were prepared according to the published procedure,[1] difluorobenzophenone **2.27** was obtained from Aldrich Chemical Co., 1,3-bis(4-fluorobenzoyl)benzene **2.29** was prepared according to published procedure.[26] 2,2',3,3'-Tetrahydro-3,3,3',3'-tetramethyl-1,1'-spiro[1H-indene]-6,6' diol **2.7a** and 3,3'-bis(4-hydroxyphenyl)pentane **2.7f**, were kindly supplied from the General Electric Company. 4,4'-Thiodiphenol **2.7b** and 2,2-bis(4-hydroxyphenyl)propane **2.7c** were obtained from Aldrich Chemical Co. 9,9-Bis(4-hydroxyphenyl)fluorene **2.7d**, and 2,2-bis(4-hydroxyphenyl)hexafluoropropane **2.7e** were obtained from Kennedy & Klim, Inc., NJ. Hydrazine hydrate, and DBU were obtained from Aldrich Chemical Co..

Synthesis of cyclo-poly[oxy-6,6'-(3,3,3,'3'-tetramethyl-2,2',3,3'-tetrahydro-1,1-spirobiindenylene)oxy-1,4-phenylene-carbonyl-1,2-phenylene-carbonyl-1,4-phenylene] 2.8a. The cyclization reaction was conducted in a 500 mL three-neck round bottom flask which was equipped with a nitrogen inlet, thermometer, Dean-Stark trap and condenser. 1,2-Bis(4-fluorobenzoyl)benzene **2.4** (8.0 g, 25 mmol), SBI **2.7a** (7.67g, 25 mmol), potassium carbonate (7.52 g, 54.4 mmol), DMAc (240 mL) and toluene (120 mL) were added. The resulting mixture was refluxed for 6 h, keeping the temperature in the range of 138-140 °C. The reaction mixture was cooled and filtered to remove the salts. The solution was then poured into methanol (1 L). The desired cyclic oligomer **2.8a** (80 % yield, 12.2g), precipitated out as a white powder and was collected by suction filtration. The product was dried in a vacuum oven (120 °C) for 12 h.



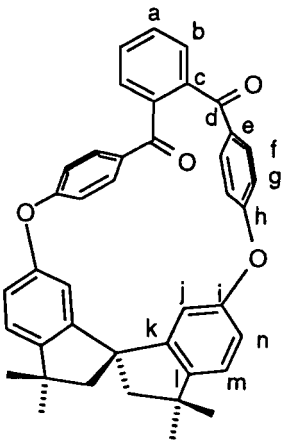
2.8a

MALDI-TOF-MS data of cyclic oligomer **2.8a** using dithranol as matrix and $AgCF_3CO_2$ as cationization agent.

Signal(m/e)	Rel. Intensity(%)	Assignment [a]	Calculated m/e	Deviation (Da)[b]
698	100	M_1+Ag	698	0
1289	33	M_2+Ag	1289	0
1879	20	M_3+Ag	1880	- 1
2471	10	M_4+Ag	2471	0
3059	2	M_5+Ag	3061	- 1
3651	1	M_6+Ag	3652	- 1
4240	1	M_7+Ag	4243	- 3

[a] M_x represent the molecular ion with x repeating units, average molecular weight calculated for repeating unit $C_{41}H_{34}O_4$ = 590.7, [b] deviation = experimental value - calculated value.

Isolation of cyclic monomer 2.8a(n=1). Cyclic monomer of **2.8a(n=1)** (0.64 g) was separated from a mixture of cyclic oligomer **2.8a** (3.5 g) by flash column chromatography using petroleum ether /diethyl ether (1:1) mixed solvent system. mp 352-3 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.39 (s, 12H, Me), 2.16 (d, J = 13 Hz, 2H, CH_2), 2.47 (d, J = 13 Hz, 2H, CH_2), 6.33 (d, J = 2 Hz, 2H, H-j), 6.40 (d, J = 9 Hz, 4H-g), 6.93 (dd, J = 2, 8 Hz, 2H, H-n), 7.18 (d, J = 8 Hz, 2H, H-m), 7.36 (d, J = 9 Hz, 4H, H-f), 7.69 (m, 4H, H-a &b); ^{13}C NMR (67.80 MHz, $CDCl_3$) δ 30.43 (Me), 31.97 (Me), 43.90 (CH_2), 57.93 , 58.97, 116.18 (C-g), 118.13 (C-j), 121.82 (C-n), 123.78 (C-m), 130.02 (C-b), 131.33 (C-a), 131.61 (C-f), 132.00 (C-e), 139.36 (C-c), 150.63, 153.30, 154.75, 164.75 , 164.40, 195.17 (C=O). MS (FAB) m/e 591(MH^+).

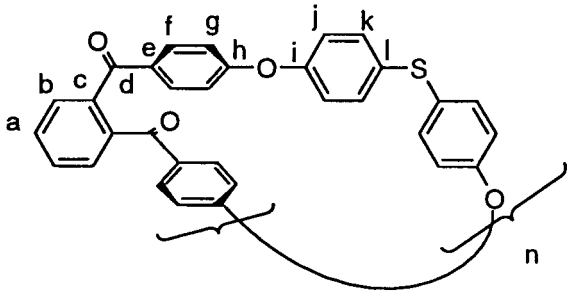


2.8a(n=1)

General procedure for synthesis of cyclic oligomers. The synthesis of cyclic oligomer **2.8b** is used as an example. The cyclization reaction was conducted in a 3 L three-neck round bottom flask which was equipped with a nitrogen inlet, thermometer, Dean-Stark trap, and condenser. The flask was charged with 1.5 L of DMF, 150 mL of toluene, and 150 g of potassium carbonate. The solution was mechanically stirred and heated to reflux. The temperature range of the refluxing solution was 145-8 °C. A solution of 4,4'-thiodiphenol **2.7b** (16.26 g, 74 mmol) and 1,2-bis(4-fluorobenzoyl)benzene **2.4** (24 g, 74 mmol) in 120 mL of DMF was added over an 8 h period via syringe pump. After the addition was completed, the resulting solution was refluxed for another 8 h. The reaction mixture was cooled and filtered to remove all the salt. The solvent was then removed from the filtrate under reduced pressure. The residue was dissolved in 300 mL of hot chloroform and filtered through a layer of Celite. The chloroform solution was concentrated to 100 mL and added to vigorously stirred methanol (300 mL) via a dropping funnel. The desired oligomers precipitated as a pale-green solid in the methanol. The precipitate was filtered, and dried in a vacuum oven (120 °C) for 12h.

The yield of **2.8b** was 34 g (90% yield). A similar procedure was applied for the preparation of other cyclic oligomers **2.8c**, **2.8d**, **2.9b**, **2.9c**, **2.9d**, **2.9e**, **2.9f**, **2.28b**, and **2.28c**. Yields of the products are shown in Table 2.1, and all of them were isolated as solid powder.

Cyclo-poly(oxy-1,4-phenylenethio-1,4-phenyleneoxy-1,4-phenylene-carbonyl-1,2-phenylenecarbonyl-1,4-phenylene) 2.8b. ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.88-7.00 (m, 8H, H-g & H-j), 7.30-7.38 (m, 4H, H-k), 7.55- 7.75 (m, 8H, H-a, b & f); ^{13}C NMR (125 MHz, $CDCl_3$) δ 117.5 (C-g), 120.5 (C-j), 129.3 (C-a), 130.0-130.5 (C-b), 131.2 (C-l), 131.9-132.5 (C-e & f), 132.8 (C-k), 139.8 (C-c), 155.0 (C-i), 161.1 (C-h), 195.2 (C-d).



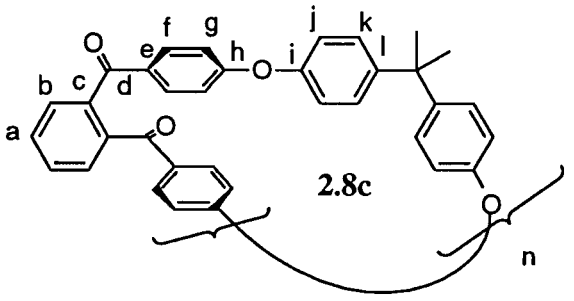
2.8b

Isolation of cyclic dimer 2.8b(n=2). Cyclic oligomeric mixture **2.8b** (13 g) was recrystallized from benzene (100 mL) to afford the desired macrocycle **2.8b(n=2)** (4.5 g, 35% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.89 (d, J = 8.8 Hz, 8H), 6.90 (d, J = 8.8 Hz, 8H), 7.32 (d, J = 8.8 Hz, 8H), 7.60-7.68 (m, 16H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 117.63, 120.47, 129.34, 130.60, 131.25, 131.96, 132.50, 132.79, 139.72, 155.08, 161.11, 195.12; mp (DMF) 263-4 °C; MS (FAB) m/z 1001(MH^+).

X-ray Structure Determination of 2.8(n=2) crystallized from DMF $C_{64}H_{40}O_8S_2 \cdot C_3H_7NO$: The crystal dimensions are 0.500 x 0.100 x 0.075 mm, measured at 21°C on a Rigaku AFC6S diffractometer with graphite monochromated Cu K_α radiation. Monoclinic, a = 25.864(3) Å, b = 15.849(5) Å, c = 13.383(5) Å, β = 95.55(2)°, V = 5460(3) Å^3, space group $C2/c$ (No.15), Z = 4, D_C = 1.307 gcm^{-3}, μ(CuKα)= 13.42 cm^{-1}, $2\theta_{max}$ = 120 °, 8461 reflections which were collected, 4236 were unique of which 1965 observed (I > 3σ(I)) and 347 parameters for the refinement with R =0.056 R_W =0.067.

Calculations were performed using the TEXSAN crystallographic software package of Molecular Structure Corporation. The structure was solved by direct methods and refined by full matrix least-squares. The non-hydrogen atoms were refined anisotropically.

Cyclo-poly(oxy-1,4-phenylene-isopropylidene-1,4-phenyleneoxy-1,4-phenylene-carbonyl-1,2-phenylenecarbonyl-1,4-phenylene) 2.8c. ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.70 (s, 6H, Me), 6.85-6.96 (m, 8H, Hg & j), 7.20-7.25 (m, 4H, H-k), 7.55-7.72 (m, 8H, H-a, b & f); ^{13}C NMR (125 MHz, $CDCl_3$) δ 30.9 (Me), 42.3 (CMe_2), 117.0 (C-g), 119.5 (C-j), 128.3 (C-k), 129.3 (C-a), 130.0-130.4 (C-b), 131.6-132.2 (C-e & f), 139.8 (C-c), 146.8 (C-l), 153.2 (C-i), 161.9 (C-h), 195.2 (C-d).

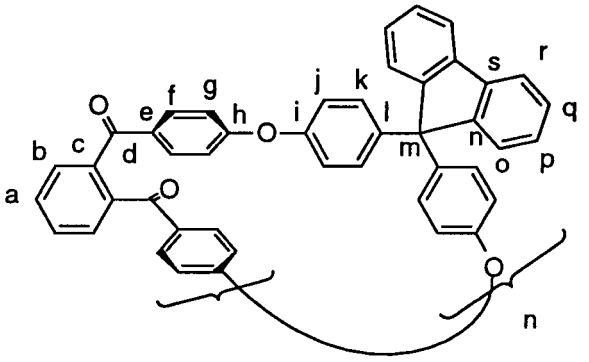


MALDI-TOF-MS data of cyclic oligomer **2.8c** using dithranol as matrix.

Signal(m/e)	Rel. Intensity(%)	Assignment [a]	Calculated m/e	Deviation (Da)[b]
1006	30	M_2-O	1005	+1
1022	100	M_2+H	1022	0
1516	15	M_3-O	1516	0
1533	40	M_3+H	1533	0
2027	8	M_4-O	2026	0
2043	10	M_4+H	2043	0
2537	4	M_5-O	2537	0
2554	4	M_5+H	2554	0
3047	2	M_6-O	3048	-1
3064	1	M_6+H	3065	-1

[a] M_x represent the molecular ion with x repeating units, average molecular weight calculated for repeating unit $C_{35}H_{26}O_4$ = 510.6, [b] deviation = experimental value - calculated value.

Cyclo-poly[oxy-1,4-phenylene-9,9-fluorenylidene-1,4-phenylene-oxy-1,4-phenylene-carbonyl-1,2-phenylenecarbonyl-1,4-phenylene] 2.8d. ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.84-6.94 (m, 8H, H-g & j), 7.18-7.25 (m, 4H, H-k), 7.25-7.46 (m, 6H, H-o, p & q), 7.52-7.64 (m, 4H, H-a & b), 7.64-7.72 (m, 4H, H-f), 7.74-7.82 (m, 2H, H-r); ^{13}C NMR (125 MHz, $CDCl_3$) δ 64.4 (C-m), 117.0-117.4 (C-g), 119.6 (C-j), 120.3 (C-r), 126.0 (C-o/p/q), 127.7 (C-o/p/q), 127.9 (C-o/p/q), 129.2 (C-a), 129.6 (C-k), 130.0-130.3 (C-b), 131.7-132.3 (C-e & f), 140.0 (C-c), 142.0 (C-l), 150.8 (C-n/s), 154.2 (C-i), 161.6 (C-h), 195.2 (C-d).



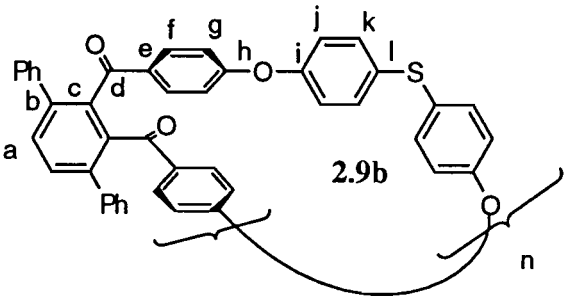
2.8d

MALDI-TOF-MS data of cyclic oligomer **2.8d** using dithranol as matrix and $AgCF_3CO_2$ as cationization agent.

Signal(m/e)	Rel. Intensity(%)	Assignment [a]	Calculated m/e	Deviation (Da)[b]
1372	100	M_2+Ag	1373	- 1
2005	43	M_3+Ag	2006	- 1
2638	18	M_4+Ag	2639	- 1
3270	7	M_5+Ag	3271	- 1
3905	2	M_6+Ag	3904	+ 1
4536	1	M_7+Ag	4537	- 1

[a] M_x represent the molecular ion with x repeating units, average molecular weight calculated for repeating unit $C_{45}H_{28}O_4$ = 632.7, [b] deviation = experimental value - calculated value.

Cyclo-poly[oxy-1,4-phenylenethio-1,4-phenyleneoxy-1,4-phenylene-carbonyl(3,6-diphenyl-1,2-phenylene)-carbonyl-1,4-phenylene] 2.9b. ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.70-6.76 (m, 4H, H-g), 6.76-6.86 (m, 4H, H-j), 7.12-7.22 (m, 6H, H-Ph), 7.22-7.32 (m, 8H, H-k & H-Ph), 7.50-7.62 (m, 6H, H-a & f); ^{13}C NMR (125 MHz, $CDCl_3$) δ 117.4 (C-g), 120.3 (C-j), 127.6 (C-Ph), 128.2 (C-Ph), 129.1 (C-Ph), 131.0 (C-a), 132.0 (C-f), 132.5 (C-l), 132.7 (C-k), 133.0 (C-e), 139.0 (C-b/c/Ph), 139.3 (C-b/c/Ph), 139.5 (C-b/c/Ph), 155.3 (C-i), 160.7 (C-h), 197.3 (C-d).

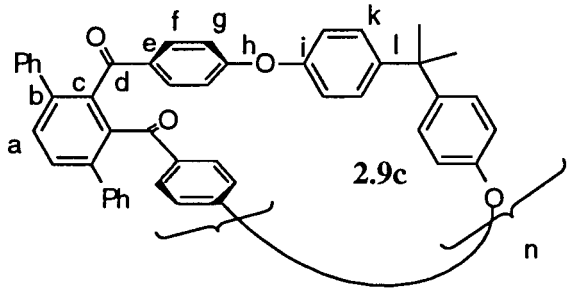


MALDI-TOF-MS data of cyclic oligomer **2.9b** using dithranol as matrix and $AgCF_3CO_2$ as cationization agent.

Signal(m/e)	Rel. Intensity(%)	Assignment [a]	Calculated m/e	Deviation (Da)[b]
1412	100	M_2+Ag	1413	- 1
2066	57	M_3+Ag	2066	0
2719	73	M_4+Ag	2719	0
3372	61	M_5+Ag	3372	0
4025	41	M_6+Ag	4024	+ 1
4678	16	M_7+Ag	4677	+ 1
5330	8	M_8+Ag	5330	0
5983	2	M_9+Ag	5983	0
6635	1	M_{10}+Ag	6636	- 1

[a] M_x represent the molecular ion with x repeating units, average molecular weight calculated for repeating unit $C_{44}H_{28}O_4S$ = 652.8, [b] deviation = experimental value - calculated value.

Cyclo-poly[oxy-1,4-phenylene-isopropylidene-1,4-phenyleneoxy-1,4-phenylene-carbonyl-(3,6-diphenyl-1,2-phenylene)carbonyl-1,4-phenylene] 2.9c. ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.70 (s, 6H, Me), 6.64-6.75 (m, 4H, H-g), 6.75-6.84 (m, 4H, H-j), 7.12-7.25 (m, 10H, H-k & H-Ph), 7.25-7.35 (m, 4H, H-Ph), 7.50-7.60 (m, 6H, H-a & f); ^{13}C NMR (125 MHz, $CDCl_3$) δ 30.0 (Me), 42.3 (CMe_2), 116.9 (C-g), 119.3 (C-j), 127.5 (C-Ph), 128.2 (C-Ph & C-k), 129.1 (C-Ph), 130.8 (C-a), 131.9 (C-f), 132.5 (C-e), 139.0 (C-b/c/Ph), 139.4 (C-b/c/Ph), 146.5 (C-l), 153.4 (C-i), 161.5 (C-h), 197.0 (C-d).

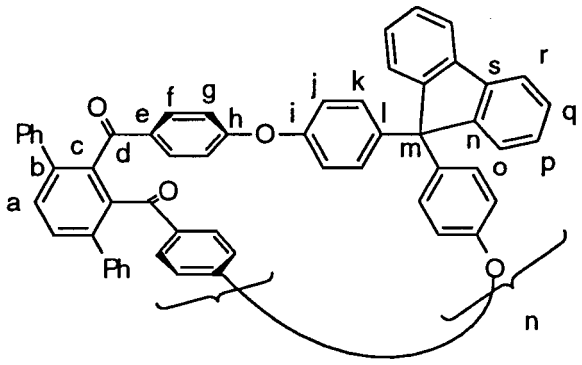


MALDI-TOF-MS data of cyclic oligomer **2.9c** using dithranol as matrix and $AgCF_3CO_2$ as cationization agent.

Signal(m/e)	Rel. Intensity(%)	Assignment[a]	Calculated m/e	Deviation (Da)[b]
1433	100	M_2+Ag	1433	0
2095	47	M_3+Ag	2096	- 1
2758	26	M_4+Ag	2759	- 1
3421	13	M_5+Ag	3422	- 1
4083	5	M_6+Ag	4084	- 1
4745	2	M_7+Ag	4747	- 2
5410	1	M_8+Ag	5410	0
6074	1	M_9+Ag	6073	+ 1

[a] M_x represent the molecular ion with x repeating units, average molecular weight calculated for repeating unit $C_{47}H_{34}O_4$ = 662.8, [b] deviation = experimental value - calculated value.

Cyclo-poly[oxy-1,4-phenylene-9,9-fluorenylidene-1,4-phenylene-oxy-1,4-phenylene-carbonyl(3,6-diphenyl-1,2-phenylene)carbonyl-1,4-phenylene] 2.9d. ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.68-6.74 (m, 4H, H-g), 6.74-6.78 (m, 4H, H-j), 7.12-7.42 (m, 20H, ArH), 7.50-7.62 (m, 6H, H-a & f), 7.74-7.82 (m, 2H, H-r); ^{13}C NMR (125 MHz, $CDCl_3$) δ 64.4 (C-m), 117.2 (C-g), 119.4 (C-j), 120.3 (C-r), 126.0 (C-o/p/q), 127.5 (C-o/p/q), 127.7 (C-Ph), 127.8 (C-o/p/q), 128.2 (C-Ph), 129.1 (C-Ph), 129.5 (C-k), 130.9 (C-a), 132.0 (C-f), 132.6 (C-e), 139.0 (C-b/c/Ph), 139.3 (C-b/c/Ph), 139.5 (C-b/c/Ph), 140.0 (C-n/s), 141.7 (C-l), 150.9 (C-n/s), 154.5 (C-i), 161.1 (C-h), 197.1 (C-d).



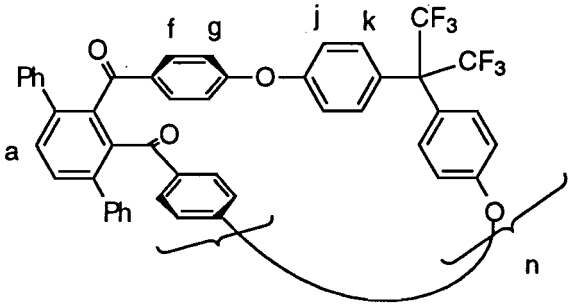
2.9d

MALDI-TOF-MS data of cyclic oligomer **2.9d** using dithranol as matrix and $AgCF_3CO_2$ as cationization agent.

Signal(m/e)	Rel. Intensity(%)	Assignment[a]	Calculated m/e	Deviation (Da)[b]
1678	100	M_2+Ag	1678	0
2463	42	M_3+Ag	2463	0
3247	22	M_4+Ag	3247	0
4033	7	M_5+Ag	4032	+ 1
4819	1	M_6+Ag	4817	+ 2
5600	0.5	M_7+Ag	5602	- 2

[a] M_x represent the molecular ion with x repeating units, average molecular weight calculated for repeating unit $C_{57}H_{36}O_4$ = 784.9, [b] deviation = experimental value - calculated value.

Cyclo-poly[oxy-1,4-phenylene-(hexafluoro-isopropylidene)-1,4-phenylene-oxy-1,4-phenylenecarbonyl(3,6-diphenyl-1,2-phenylene)-carbonyl-1,4-phenylene] 2.9e. ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.76-6.82 (m, 4H, H-g), 6.84-6.90 (m, 4H, H-j), 7.12-7.24 (m, 6H, Ph), 7.27-7.38 (m, 8H, H-k & Ph), 7.56-7.64 (m, 6H, H-a & f).



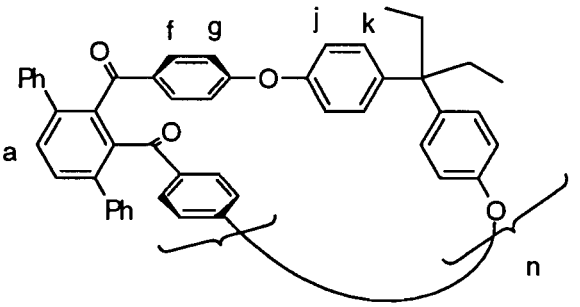
2.9e

MALDI-TOF-MS data of cyclic oligomer **2.9e** using dithranol as matrix and $AgCF_3CO_2$ as cationization agent.

Signal(m/e)	Rel. Intensity(%)	Assignment[a]	Calculated m/e	Deviation (Da)[b]
1649	100	M_2+Ag	1649	0
2420	36	M_3+Ag	2420	0
3190	17	M_4+Ag	3191	- 1
3961	6	M_5+Ag	3962	- 1
4731	2	M_6+Ag	4732	- 1
5503	1	M_7+Ag	5503	0

[a] M_x represent the molecular ion with x repeating units, average molecular weight calculated for repeating unit $C_{47}H_{28}F_6O_4$ = 770.7, [b] deviation = experimental value - calculated value.

Cyclo-poly[oxy-1,4-phenylene-3,3-pentanylidene-1,4-phenylene-oxy-1,4-phenylene-carbonyl(3,6-diphenyl-1,2-phenylene)carbonyl-1,4-phenylene] 2.9f. ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.62 (m, 6H, CH_3), 2.08 (m, 4H, CH_2), 6.63-6.74 (m, 4H, H-g), 6.74-6.84 (m, 4H, H-j), 7.07-7.32 (m, 14H, H-k &Ph), 7.48-7.60 (m, 6H, H-a & f).



2.9f

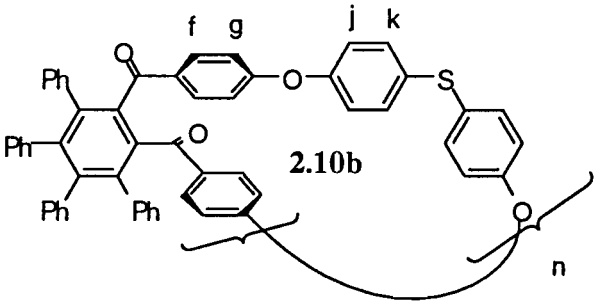
MALDI-TOF-MS data of cyclic oligomer **2.9f** using dithranol as matrix and $AgCF_3CO_2$ as cationization agent.

Signal(m/e)	Rel. Intensity(%)	Assignment[a]	Calculated m/e	Deviation (Da)[b]
1489	58	M_2+Ag	1490	- 1
2180	80	M_3+Ag	2180	0
2872	100	M_4+Ag	2871	+ 1
3563	59	M_5+Ag	3562	+ 1
4253	21	M_6+Ag	4253	0
4945	4	M_7+Ag	4944	+ 1

[a] M_x represent the molecular ion with x repeating units, average molecular weight calculated for repeating unit $C_{49}H_{38}O_4$ = 690.8, [b] deviation = experimental value - calculated value.

Cyclo-poly[oxy-1,4-phenylenethio-1,4-phenyleneoxy-1,4-phenylene-carbonyl(3,4,5,6-tetraphenyl-1,2-phenylene)-carbonyl-1,4-phenylene]

2.10b. The cyclization reaction was conducted in a 100 mL three-neck round bottom flask which was equipped with a nitrogen inlet, thermometer, Dean-Stark trap, and condenser. The flask was charged with 80 mL of DMF, 10 mL of toluene, 4,4'-thiodiphenol **2.7b** (0.5 g, 2.29 mmol), difluoro-monomer **2.6** (1.44 g, 2.29 mmol.) and 5 g of potassium carbonate. The solution was magnetically stirred and heated to reflux. The temperature range of the refluxing solution was 145-8 °C. The resulting solution was refluxed for another 16 h. The reaction mixture was filtered while it was still hot to remove the salts. The solvent was then removed from the filtrate under reduced pressure. The residue was extracted with ethyl acetate (50 mL) using a soxhlet apparatus for 24 h. Evaporation of the ethyl acetate gave the desired oligomer **2.10b** (700 mg, 36 % yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.70-7.00 (m, 28H, ArH), 7.22-7.32 (m, 4H, H-k), 7.54-7.64 (m, 4H, H-f).



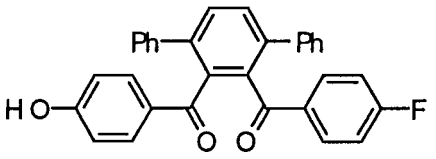
2.10b

MALDI-TOF-MS data of cyclic oligomer **2.10b** using dithranol as matrix and $AgCF_3CO_2$ as cationization agent.

Signal(m/e)	Rel. Intensity(%)	Assignment[a]	Calculated m/e	Deviation (Da)[b]
1718	100	M_2+Ag	1718	0
2523	47	M_3+Ag	2523	0
3328	27	M_4+Ag	3328	0
4133	17	M_5+Ag	4133	0
4939	8	M_6+Ag	4938	+1
5743	3	M_7+Ag	5743	0

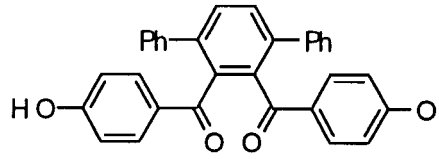
[a] M_x represent the molecular ion with x repeating units, average molecular weight calculated for repeating unit $C_{56}H_{36}O_4$ = 805.0, [b] deviation = experimental value - calculated value.

1-(4-Hydoxybenzoyl)-2-(4-fluorobenzoyl)-3,6-diphenylbenzene 2.20. 1,2-Bis(4-fluorobenzoyl)-3,6-diphenylbenzene **2.5** (5 g, 10.8 mmol) was dissolved in DMSO (50 mL), and followed by KOH (0.89 g, 15.9 mmol) in water (7.5 mL). The resulting solution was refluxed for 15 min, and was poured into 1 M HCl (500 mL) giving a precipitate which was filtered. The solid was then dissolved in ether (300 mL) and was extracted with 5% KOH solution (2 x 300 mL). The combined KOH layer was acidified with conc HCl. The solid precipitate was collected by filtration. Recrystallization of the solid from ethanol gave the desired monomer **2.20** (2.30 g) mp 251-2 °C; ^{1}H NMR (200 MHz, DMSO-d_6) δ 10.33 (s, 1H), 7.70 (s, 2H), 7.52 (dd, J=8.6, 5.3 Hz, 2H), 7.37 (d, J=8.6 Hz, 2H), 7.31 - 7.17 (m, 10H), 7.05 (dd, J=8.6 Hz, 2H), 6.59 (d, J=8.6 Hz, 2H); ^{13}C NMR (67.8 MHz, DMSO-d_6) δ 197.25, 196.52, 167.52, 163.81, 163.09, 140.27, 140.06, 139.93, 139.67, 138.78, 134.94, 134.91, 133.28, 133.12, 133.07, 132.39, 131.94, 129.93, 129.85, 129.78, 129.36, 129.29, 128.76, 128.65, 116.37, 116.05, 115.90; MS (EI) *m/e* 472(M^+).



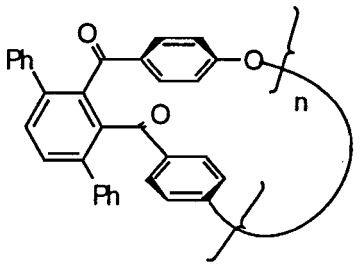
2.20

1,2-Bis(4-hydoxybenzoyl)-3,6-diphenylbenzene 2.21. 1,2-Bis(4-fluorobenzoyl)-3,6-diphenylbenzene **2.5** (5 g, 10.8 mmol) was dissolved in DMSO (50 mL), and followed by the addition of KOH (4.8 g, 85.7 mmol) in water (10 mL). The resulting solution was refluxed for 30 min, was allowed to cool to room temperature and was neutralized with 1 M hydrochloric acid. The solid precipitate was collected by filtration. Recrystallization of the solid from DMSO gave the desired monomer **2.21** (4.0g, 80% yield). mp 370-1 °C; ^{1}H NMR (500 MHz, DMSO-d_6) δ 10.25 (s, 2H), 7.65 (s, 2H), 7.31 (d, J=8.8 Hz, 4H), 7.17 - 7.28 (m, 10H), 6.55 (d, J=7.3 Hz, 4H); ^{13}C NMR (50 MHz, DMSO-d_6) δ 196.95, 163.35, 140.79, 140.06, 139.68, 133.35, 132.13, 130.15, 129.56, 128.86, 116.08; MS (EI) *m/e* 470.7 (M^+).



2.21

Cyclo-poly[oxy-1,4-phenylene-carbonyl-(3,6-diphenyl-1,2-phenylene) -carbonyl-1,4-phenylene] 2.22. The cyclization reaction was conducted in a 50 mL three-neck round bottom flask which was equipped with a nitrogen inlet, thermometer, Dean-Stark trap, and condenser. The flask was charged with 20 mL of DMF, 3 mL of toluene, and 2 g of potassium carbonate. The solution was magnetically stirred and heated to reflux. The temperature range of the refluxing solution was 145-8 °C. A solution 1-(4-hydoxybenzoyl)-2-(4-fluorobenzoyl)-3,6-diphenylbenzene **2.20** (630 mg, 1.33 mmol.) in 5 mL of DMF was added over an 8 h period via syringe pump. After the addition was completed, the resulting solution was refluxed for another 8h. The reaction mixture was filtered while hot to remove the salts. The solvent was then reduced to 10 mL under reduced pressure and added into vigorously stirred methanol (30 mL). The desired oligomer **2.22** precipitated as a white solid in the methanol. The precipitate was filtered, and dried in a vacuum oven (120 °C) for 12 h. The yield of **2.22** was 500 mg (80 % yield).



2.22

MALDI-TOF-MS data of cyclic oligomer **2.22** using dithranol as matrix.

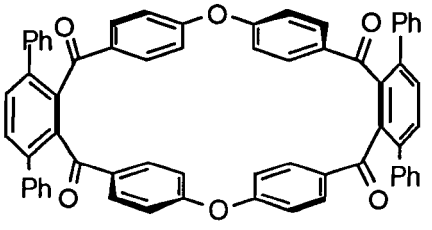
Signal(m/e)	Rel. Intensity(%)	Assignment[a]	Calculated m/e	Deviation (Da)[b]
906	100	M_2+H	906	0
1358	65	M_3+H	1359	- 1
1794	65	M_4-O	1794	0
2246	35	M_5-O	2247	- 1
2700	15	M_6-O	2699	+ 1
3170	10	M_7+H	3169	+ 1
3622	5	M_8+H	3621	+ 1

[a] M_x represent the molecular ion with x repeating units, average molecular weight calculated for repeating unit $C_{32}H_{20}O_3$ = 452.5, [b] deviation = experimental value - calculated value.

Linear polymeric analogue of 2.22, poly[oxy-1,4-phenylene-carbonyl-(3.6-diphenyl-1,2-phenylene)carbonyl-1,4-phenylene]. The polymerization reaction was conducted in a 50 mL three-neck round bottom flask which was equipped with a nitrogen inlet, thermometer, Dean-Stark trap and condenser. The

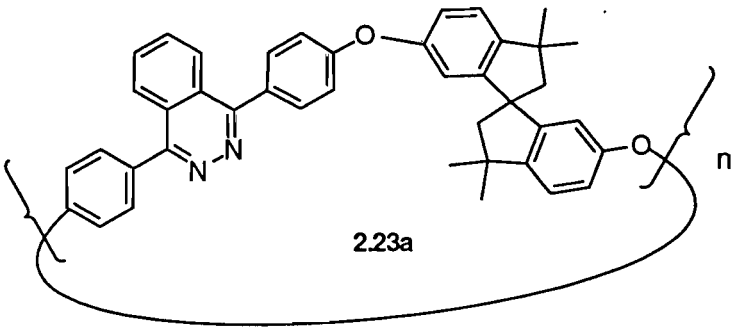
reaction vessel was charged with difluoro-monomer **2.5** (1.01 g, 2.1 mmol), dihydroxy monomer **2.21** (1.00g, 21 mmol), potassium carbonate (0.5g), DMAc (8 mL) and toluene (4 mL). The resulting mixture was refluxed for 3 h, and the temperature was raised to 165 °C by removing toluene. The reaction mixture was kept at 165 °C for 48 h whereupon the polymer precipitate from the mixture. The reaction mixture was cooled and filtered. The crude product was dissolved in hot NMP (10 mL), and was filtered, and precipitated into MeOH (50 mL) to yield the desired polymer (1.6 g, 80 % yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.62 (s, 2H), 7.57 (d, J=7.5 Hz, 4H), 7.29 (d, J=7 Hz, 4H), 7.20 (m, 6H), 6.63 (d, J=7.5 Hz, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 197.40, 159.77, 139.64, 139.30, 139.22, 133.51, 131.86, 131.02, 129.17, 128.23, 127.57, 118.11. Mw = 40 kg/mol; Mn = 16 kg/mol. Inherent viscosity ($CHCl_3$, 25°C) = 0.33 dL/g.

Isolation of cyclo-bis[oxy-1,4-phenylene-carbonyl-(3,6-diphenyl-1,2-phenylene)-carbonyl-1,4-phenylene] 2.22(n=2). The mixture of cyclic oligomer **2.22** (500 mg) was refluxed with chloroform (5 mL) in a test tube for 2 min, and the hot solution was filtered under suction. The residue was the desired cyclic dimer **2.22(n=2)** (200 mg), and was collected and dried in vacuum oven for 12h. mp 415 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.68 (s, 2H), 7.44 (d, J=8.3 Hz, 4H), 7.37 (d, J=7.8 Hz, 4H), 7.25 - 7.30 (m, 6H), 6.51 (d, J=8.3 Hz, 4H); MS(FAB) *m/e* 905 ($M+H^+$).



2.22(n=2)

Cyclo-poly[1,4-phthalazinylene-1,4-phenyleneoxy-6,6'-(3,3,3,'3'-tetramethyl-2,2',3,3'-tetrahydro-1,1'-spirobiindenylene)-oxy-1,4-phenylene] 2.23a. Cyclic oligomer **2.8a** (16g) was refluxed with 50 mL of chloroform for 30 min. Then the solution was allowed to stand at room temp for 2 h. At this time the cyclic monomer **2.8a(n=1)** was precipitated out and was removed by suction filtration. Evaporation of the filtrate gave the desired oligomer mixture (6.5 g) that has 3 wt% of cyclic monomer. To a solution of monocyclic depleted cyclic oligomer **2.8a** (2 g) in dioxane (20 mL) was added hydrazine hydrate (2 mL) and conc HCl acid (0.6 mL). The resulting solution was refluxed for 3 h. A green solid precipitated out during the reflux. The solid was filtered, redissolved in acetic acid (20 mL), followed by the addition of sodium nitrite (3 g). The solution was refluxed for 15 min and was coagulated in water (20 mL) and filtered. The residue was redissolved in chloroform, and filtered. The chloroform solution was concentrated and then coagulated in methanol (50 mL). The green solid was filtered and dried under vacuum at 120 °C overnight to give the desired product **2.23a** in 90% yield. M_n = 1.8 kg/mol, M_w = 3.7 kg/mol.



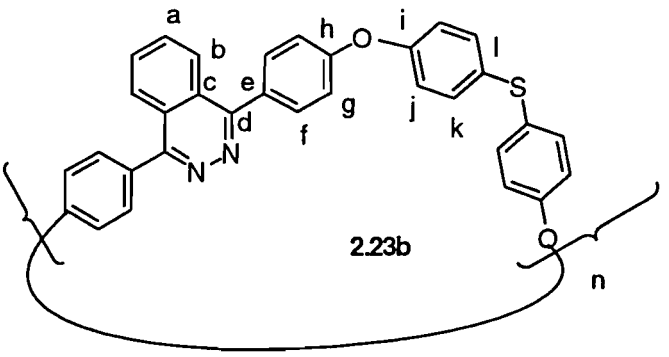
2.23a

MALDI-TOF-MS data of cyclic oligomer **2.23a** using dithranol as matrix and $AgCF_3CO_2$ as cationization agent.

Signal(m/e)	Rel. Intensity(%)	Assignment[a]	Calculated m/e	Deviation (Da)[b]
1281	100	M_2+Ag	1281	0
1867	70	M_3+Ag	1868	- 1
2454	80	M_4+Ag	2455	- 1
3042	38	M_5+Ag	3042	0
3629	16	M_6+Ag	3628	+ 1
4214	5	M_7+Ag	4215	- 1

[a] M_x represent the molecular ion with x repeating units, average molecular weight calculated for repeating unit $C_{41}H_{34}N_2O_2$ = 586.7 [b] deviation = experimental value - calculated value.

Cyclo-poly(1,4-phthalazinylene-1,4-phenyleneoxy-1,4-phenylene-thio-1,4-phenyleneoxy-1,4-phenylene) 2.23b. To a solution of cyclic oligomer **2.8b** (2 g) in dioxane (10 mL) was added hydrazine hydrate (0.5 mL) and conc HCl acid (0.15 mL). The resulting solution was refluxed for 2 h. A green solid precipitated out during heating. The reaction mixture was diluted with methanol (20 mL), and the green solid was filtered and dried under vacuum for 12 h to give the desired cyclic oligomers **2.23b** (1.9 g, 95% yield). The same procedure was followed for the synthesis for **2.23c** from **2.8c**. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.08 (d, J=8.3 Hz, 4H, H-j), 7.16 (d, J = 8.3Hz, H-g of dimer), 7.22 (m, H-g), 7.39 (m, 4H, H-k), 7.76 &7.80 (d, J = 8.3 Hz, 4H, H-f), 7.83 & 7.87 (m, 2H, H-a), 8.10 & 8.17 (m, 2H, H-b); ^{13}C NMR (125 MHz, $CDCl_3$) δ 118.48 (C-g), 118.80 (C-g), 118.94 (C-g), 119.85 (C-j), 120.05 (C-j), 120.60 (C-j), 125.85 (C-c), 126.49 (C-b), 130.50 (C-e), 131.18 (C-l), 131.34 (C-l), 131.79 (C-f), 131.86 (C-f), 131.98 (C-a), 132.04 (C-a), 132.88 (C-k), 133.06 (C-k), 156.16, 157.96, 158.10, 158.30, 158.54.



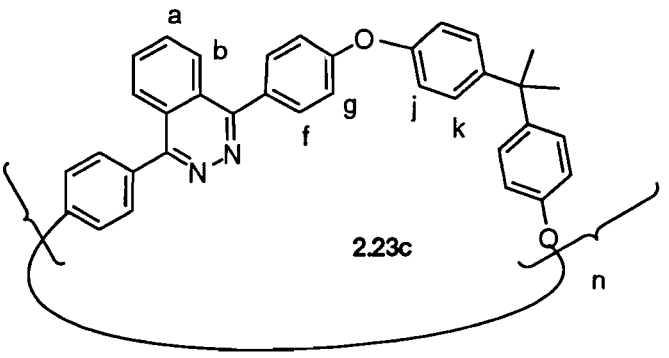
2.23b

MALDI-TOF-MS data of cyclic oligomer **2.23b** using dithranol as matrix and $AgCF_3CO_2$ as cationization agent.

Signal(m/e)	Rel. Intensity(%)	Assignment[a]	Calculated m/e	Deviation (Da)[b]
1100	100	M_2+Ag	1101	- 1
1597	25	M_3+Ag	1598	- 1
2093	15	M_4+Ag	2094	- 1
2590	4	M_5+Ag	2591	- 1
3087	1	M_6+Ag	3087	0

[a] M_x represent the molecular ion with x repeating units, average molecular weight calculated for repeating unit $C_{32}H_{20}N_2O_2S$ = 496.7, [b] deviation = experimental value - calculated value.

Cyclo-poly(1,4-phthalazinylene-1,4-phenyleneoxy-1,4-phenylene-isopropylidene-1,4-phenyleneoxy-1,4-phenylene) 2.23c. ^{1}H NMR (500 MHz, DMSO-d_6) δ 1.68-1.73 (m, 6H, Me), 7.04-7.10 (m, 4H, H-j), 7.14 (d, J = 8.3Hz, H-g of dimer), 7.20 (m, H-g), 7.30-7.36 (m, 4H, H-k), 7.72 (d, J = 8.3Hz, H-f of dimer), 7.76 (d, J = 8.3Hz, H-f), 7.90-8.10 (m, 4H, H-a & b).



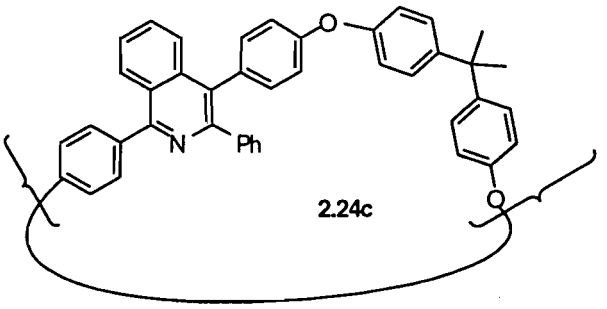
2.23c

MALDI-TOF-MS data of cyclic oligomer **2.23c** using dithranol as matrix and $AgCF_3CO_2$ as cationization agent.

Signal(m/e)	Rel. Intensity(%)	Assignment[a]	Calculated m/e	Deviation (Da)[b]
1120	100	M_2+Ag	1121	- 1
1628	16	M_3+Ag	1628	0
2135	29	M_4+Ag	2134	+ 1
2642	11	M_5+Ag	2641	+ 1
3149	5	M_6+Ag	3147	+ 2
3656	1	M_7+Ag	3654	+ 2

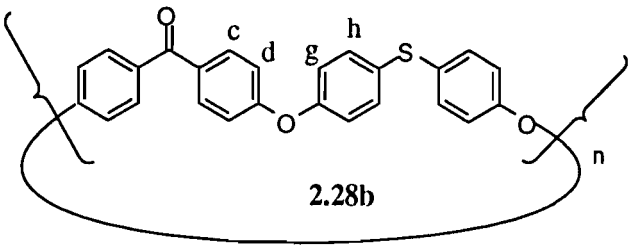
[a] M_x represent the molecular ion with x repeating units, average molecular weight calculated for repeating unit $C_{35}H_{26}N_2O_2$ = 506.6, [b] deviation = experimental value - calculated value.

Cyclo-poly[1,4-(3-phenylisoquinolinylene)-1,4-phenyleneoxy-1,4-phenylene-isopropylidene-1,4-phenyleneoxy-1,4-phenylene] 2.24c. To a solution of **2.8c** (0.5 g) in chlorobenzene(10 mL) was added benzylamine (2 mL) and 1,8-diazabicylco[5.4.0]undec-7-ene (2 mL). The resulting solution was refluxed for 30 h. The solution was coagulated in methanol (50 mL), filtered and dried under vacuum for 12 h to give **2.24c** as a green solid in 80% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.68-1.73 (m, 6H, Me), 6.92-7.00 (m, 2H), 7.00-7.12 (m, 4H),7.12-7.40 (m, 11H), 7.40-44 (m, 2H), 7.45-7.56 (m, 1H), 7.56-7.65 (m, 1H), 7.70-7.82 (m, 3H), 8.14-8.24 (m, 1H).



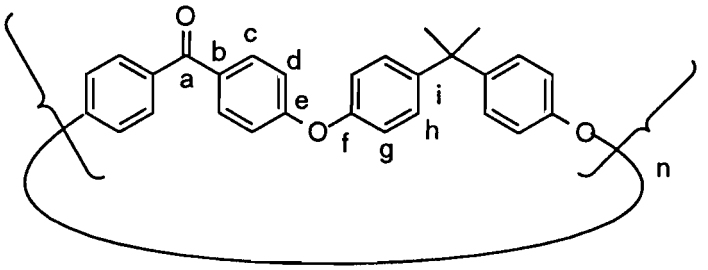
2.24c

Cyclo-poly(oxy-1,4-phenylenethio-1,4-phenyleneoxy-1,4-phenylene-carbonyl-1,4-phenylene) 2.28b. The cyclization reaction was conducted in a 3 L three-neck round bottom flask which was equipped with a nitrogen inlet, thermometer, Dean-Stark trap, and condenser. The flask was charged with 50 mL of DMF, 5 mL of toluene, and 1 g of potassium carbonate. The solution was mechanically stirred and heated to reflux. The temperature range of the refluxing solution was 145-8 °C. A solution of 4,4'-thiodiphenol **2.7b** (0.5 g, 2.29 mmol) and difluorobenzophenone **2.27** (0.5 g, 2.29 mmol.) in 5 mL of DMF was added over an 8h period via syringe pump. After the addition was completed, the resulting solution was refluxed for another 8h. The solvent was then removed under reduced pressure. The residue was refluxed with water (50 mL), filtered, and dried under vacuum for 12 h to give the desired cyclic oligomer **2.28b**. ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.98-7.06 (m, 8H, H-d & H-g), 7.32-7.40 (m, 4H, H-h), 7.55 (d, J = 8.8 Hz, H-c) & 7.79 (d, J = 8.8 Hz, H-c).



2.28b

Cyclo-poly(oxy-1,4-phenylenecarbonyl-1,4-phenyleneoxy-1,4-phenylene-isopropylidene-1,4-phenylene) 2.28c. The desired cyclic oligomer **2.28c** were prepared according to the same procedure as the synthesis of cyclic oligomer **2.28b**, using difluorobenzophenone **2.27** and BPA **2.7c** as starting materials. ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.70(s, 6H, Me), 6.95-7.05 (m, 8H, H-d & H-g), 7.22-7.28 (m, 4H, H-h), 7.71 (d, J = 8.8 Hz, H-c) & 7.78 (d, J = 8.8 Hz, H-c); ^{13}C NMR (125 MHz, $CDCl_3$) δ 30.9 (Me), 42.3 (CMe_2), 117.0 (C-d) , 119.5 (C-g), 128.3 (C-h), 132.0 –132.2 (C-b &C-c), 146.7– 146.9 (C-i), 153.4 (C-f), 161.4 (C-e), 194.2 – 194.6 (C-a).



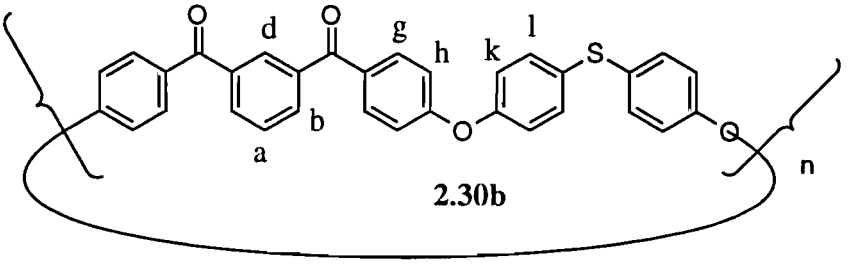
2.28c

MALDI-TOF-MS data of cyclic oligomer **2.28c** using dithranol as matrix and $AgCF_3CO_2$ as cationization agent.

Signal(m/e)	Rel. Intensity(%)	Assignment[a]	Calculated m/e	Deviation (Da)[b]
920	100	M_2+Ag	921	- 1
1326	43	M_3+Ag	1327	- 1
1732	39	M_4+Ag	1733	- 1
2139	31	M_5+Ag	2140	- 1
2545	25	M_6+Ag	2546	- 1
2952	16	M_7+Ag	2953	- 1
3358	13	M_8+Ag	3360	- 2
3765	7	M_9+Ag	3766	- 1
4170	2	M_{10}+Ag	4173	- 3

[a] M_x represent the molecular ion with x repeating units, average molecular weight calculated for repeating unit $C_{28}H_{22}O_3$ = 406.5, [b] deviation = experimental value - calculated value.

Cyclo-poly(oxy-1,4-phenylenethio-1,4-phenyleneoxy-1,4-phenylene-carbonyl-1,3-phenylenecarbonyl-1,4-phenylene) 2.30b. The cyclization reaction was conducted in a 100 mL three-neck round bottom flask which was equipped with a nitrogen inlet, thermometer, Dean-Stark trap, and condenser. The flask was charged with 50 mL of DMF, 5 mL of toluene, 4,4'-thiodiphenol **2.7b** (0.5 g, 2.29 mmol), 1,3-bis(4-fluorobenzoyl)benzene **2.29** (0.74 g, 2.29 mmol.) and 5 g of potassium carbonate. The solution was magnetically stirred and heated under reflux for 16 h at 145-8 °C. The reaction mixture was filtered immediately when it was still hot. The solvent was then removed from the filtrate under reduced pressure. The residue was dissolved in 10 mL of hot DMF and the desired oligomers precipitated as a white solid in the methanol (50 mL). The precipitate was filtered, and dried in a vacuum oven (120 °C) for 12 h. The yield of **2.30b** was 900 mg (78 % yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.00-7.08 (m, 8H, H-h & H-k), 7.34-7.42 (m, 4H, H-l), 7.58 - 7.68 (m, 1H, H-a), 7.80 - 7.86 (m, 4H, H-g), 7.96 - 8.14 (m, 3H, H-b & d).



2.30b

Melt polymerization of cyclic oligomers. Cyclic oligomer **2.8c** (0.5 g of dried powder) was dissolved into a minimum amount of chloroform, and the methanolic solution CsF (300 μL, conc.= 5 mg / mL) was added. The clear solution was evaporated, and the powder formed was further dried at 150°C under high vacuum overnight. The dried powder (50 mg) was placed in a DSC pan on a Seiko 220 TGA/DTA instrument. The powder was then heated to 340°C for 30 minutes under nitrogen with a flow rate of 200 mL/min. After cooling, the resulting material was dissolved into 10 mL of chloroform and the mixture was vigorously shaken overnight. The soluble fraction was then analyzed by GPC.

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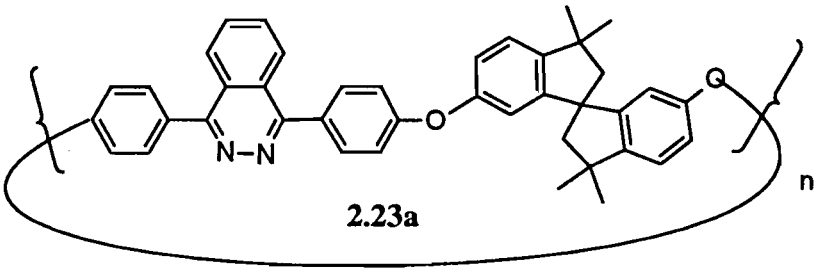
Chapter 3

Thermal Chemistry of Poly(aryl ether phthalazine)s and the Synthesis of Poly(aryl ether quinazoline)

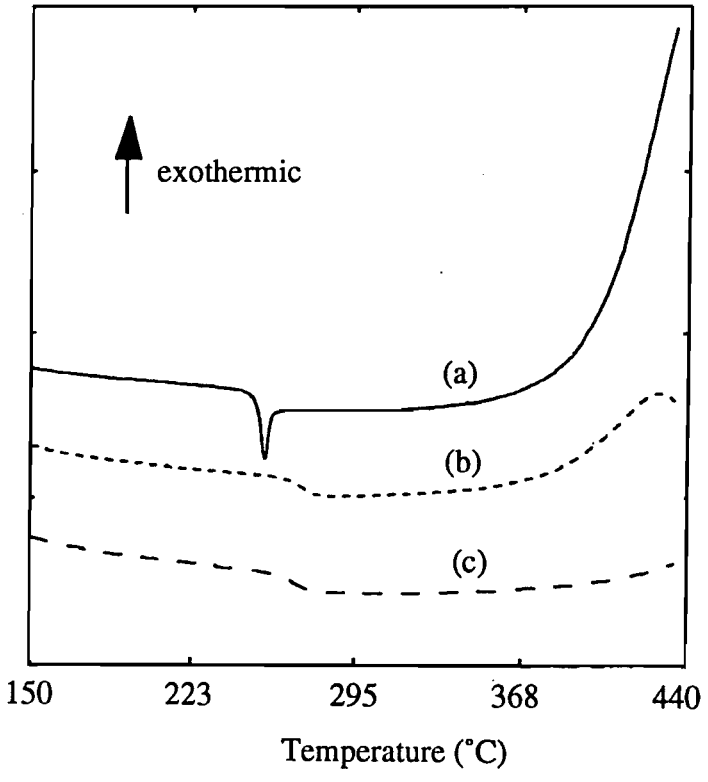
3.1 Introduction

While we were investigating the ring opening polymerization behavior of the cyclic(aryl ether phthalazine) **2.23a** we found, that without the addition of catalyst, the material became insoluble after thermal curing. Careful examination of the material by DSC indicated that an exothermic reaction occurred when the material reached 360 °C (Figure 3.1a).

Figure 3.1a. DSC traces of cyclic phthalazine oligomers **2.23a** (a) first scan, (b) second scan, (c) third scan.



2.23a



In order to further understand this phenomenon, we examined the thermal behavior of the linear high molecular weight poly(ether phthalazine)s. The synthesis of poly(ether phthalazine)s **3.4**, **3.5**, and **3.6** has been reported by Singh and Hay (Scheme 3.1). [1] Interestingly, exothermic reactions were also found to occur in these polymers when they were heated (Figure 3.1b). We speculated that the origin of the exotherm might be due to a thermal reaction of the phthalazine moiety of these polymers, which could lead to cross-linking and thus resulting in insolubility observed in the cured material. Herein, we report our studies toward the elucidation of the origin of the exothermic reaction and the physio-chemical phenomena associated with it.

Scheme 3.1

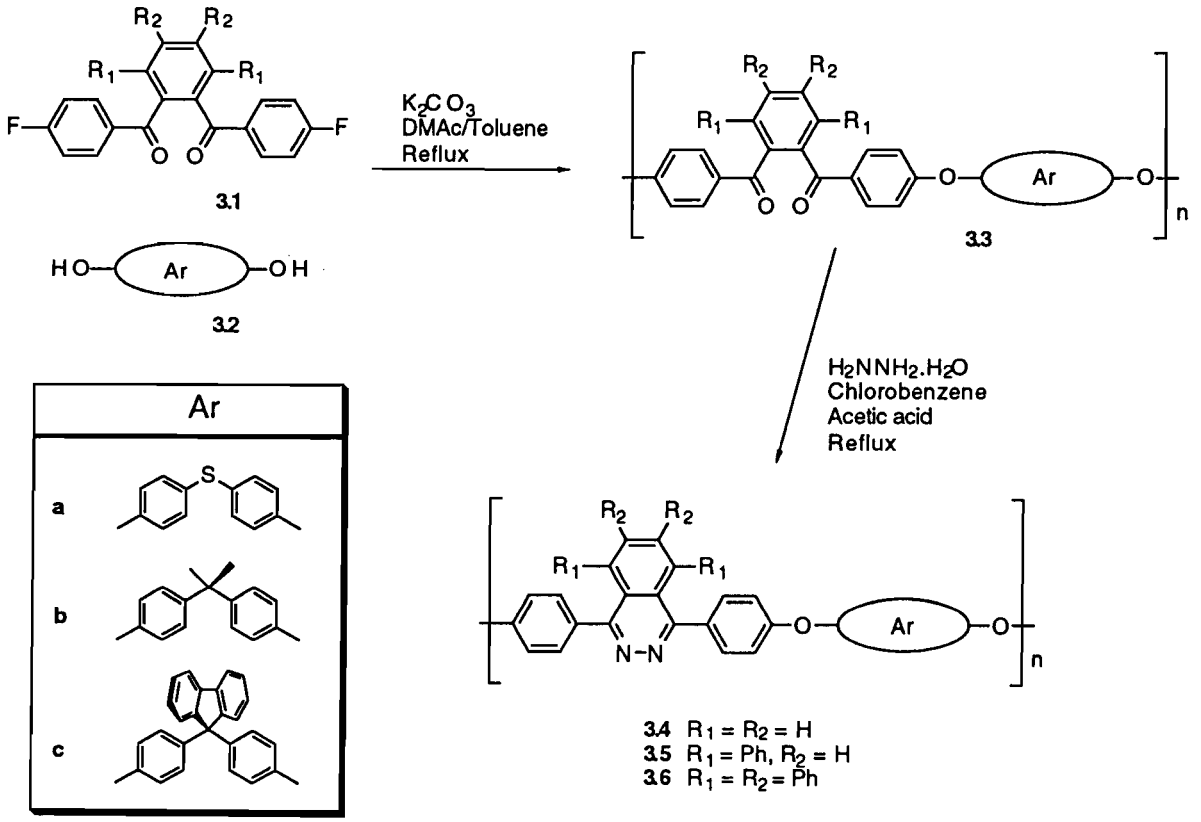
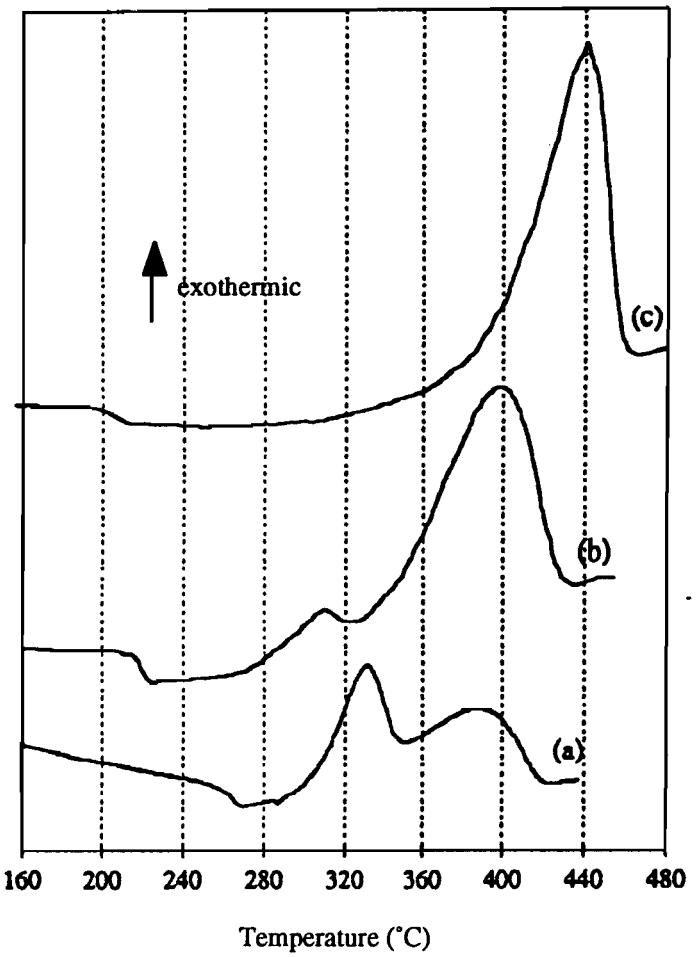


Figure 3.1b. DSC traces of poly(aryl ether phthalazine)s (a) **3.6b**, (b) **3.5a**, (c) **3.4b**.



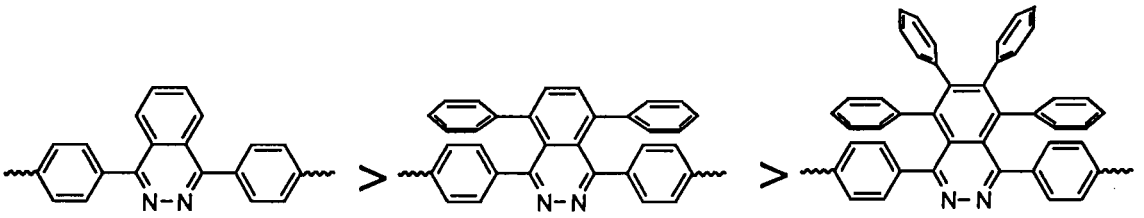
3.2 Results and discussion

Thermal analyses. The enthalpy changes of the exotherms (ΔH) observed on heating the polymers containing the phthalazine moiety were similar and were estimated to be ~ -70 kJ/mol by DSC. We found that the peak maximum temperature (T_{max}) of the exotherms varies depending on the substitution pattern of the phthalazine moiety (Figure 3.1b and Table 3.1) in the order of, diphenylphthalazine moiety **3.4** > tetraphenylphthalazine **3.5** > hexaphenylphthalazine **3.6**. This suggested that the exothermic reaction proceeds more readily in polymers **3.5** and **3.6** relative to polymer **3.4**. The more crowded the phthalazine moiety is the more readily the reaction might be expected to take place.

Table 3.1. Thermoanalyses of poly(aryl ether phthalazine)s.

Polymer	Mw (kg/mol)[a]	Tg (°C)[b]	Tg (°C)[c] after curing	ΔTg (°C)[d]	Weight loss(%)[e]	T_{max} (°C)[b]
3.4a	78	205	252	+47	<4	470
3.4b	75	225	282	+62	<4	440
3.4c	85	287	330	+43	<4	430
3.5a	70	232	248	+16	<2	400
3.5b	46	234	248	+14	<2	400
3.6b	130	267	276	+9	<2	330/387
3.6c	140	320	329	+9	<2	353

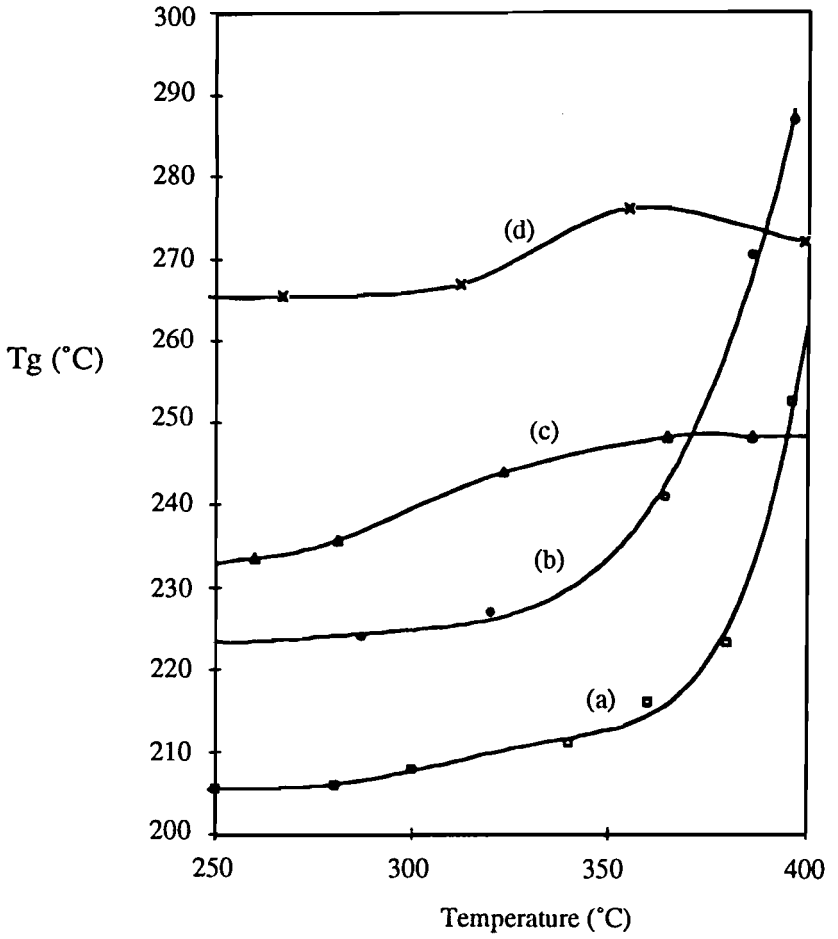
[a] Molecular weight measurements were obtained by GPC and calibration with polystyrene standards. [b] Tg and T_{max} were measured by DSC at a heating rate of 20 °C/min under nitrogen atmosphere. [c] Polymers were cured at 390 °C for 30 min under nitrogen atmosphere in a TGA instrument. [d] ΔTg = Tg after curing - Tg before curing. [e] Weight loss during the curing was obtained in a TGA instrument.



	3.4	3.5	3.6
Tmax	~440 °C	~400°C	~387°C
ΔTg	50-60 °C	~16 °C	~9°C

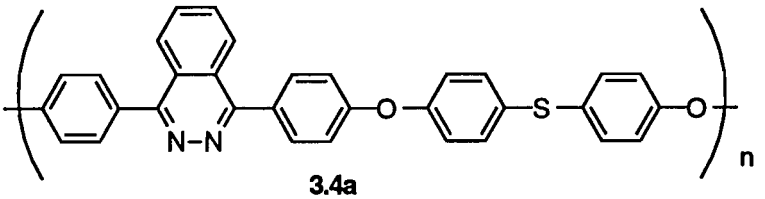
Furthermore, it was found thermal treatment of these phthalazine containing polymers resulted in an increase in their glass transition temperature (Tg) and the resulting polymers become insoluble. This suggested that the polymers underwent a cross-linking reaction (Table 3.1).

Figure 3.2. Plots of Tg against curing temperature of cured polymers (a) **3.4a**, (b) **3.4b**, (c) **3.5a**, (d) **3.6b** after curing at various temperatures for 30 min under nitrogen atmosphere.

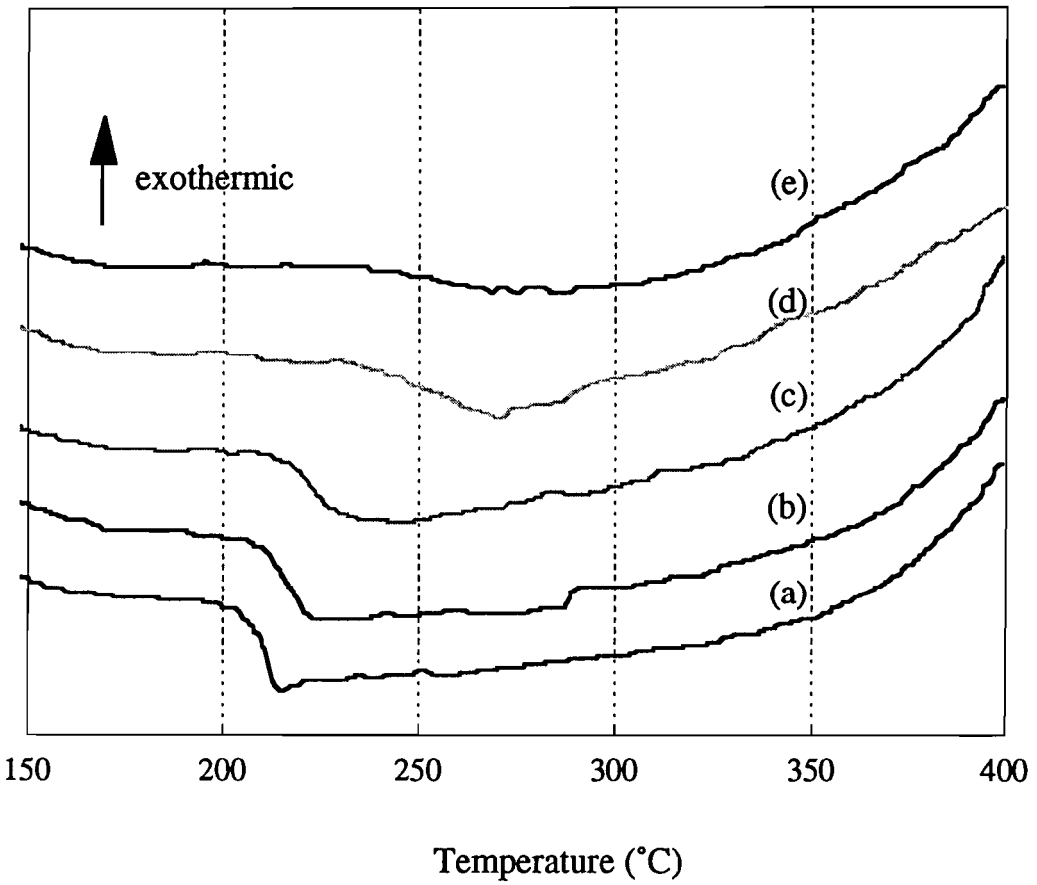


To further understand the thermal curing behavior, polymers **3.4a**, **3.4b**, **3.5a**, and **3.6b** were cured at various temperature for 30 min under nitrogen atmosphere, and the Tgs of the materials after curing were measured. A plot of Tg versus curing temperature in Figure 3.2 shows that the Tg of diphenylphthalazine containing polymers **3.4a** and **3.4b** increases rapidly as the curing temperature goes beyond 370 °C. A Tg increase up to 50 - 60 °C can be achieved if the polymers were cured at 400 °C for 30 min, or alternatively at 370 °C for 2 h. Figure 3.3 shows an overlay of the DSC traces of diphenylphthalazine containing polymer **3.4a** after curing at different temperatures and it is apparent that the change in heat capacity at the glass transition temperature (ΔCp) decreases as curing temperature increases, which is an indication of increasing cross-linking density. Thermal curing of **3.4a** and **3.4b** at 400 °C for more than 30 min resulted in the elimination of Tg.

Figure 3.3. DSC traces of polymer **3.4a** after curing at various temperatures for 30 min under nitrogen; (a) 340 °C, (b) 360 °C, (c) 380 °C, (d) 396 °C, (e) 410 °C.

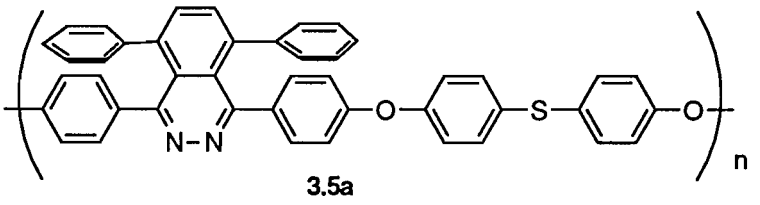


3.4a



On the other hand, the Tg of tetraphenylphthalazine containing polymer **3.5a** and hexaphenylphthalazine containing polymer **3.6b** increased only by a small amount, 16 and 9 °C respectively, and levelled off after the curing temperature reached ~360 °C (Figure 3.2), with no significant increase even when the curing temperature increased beyond 360 °C. Furthermore, the Tg increase stopped as soon as the exotherms were eliminated, and there were no further appreciable decreases in ΔCp (Figure 3.4 & 3.5).

Figure 3.4. DSC traces of polymer **3.5a** after curing at various temperatures for 30 min under nitrogen; (a) 280 °C, (b) 320 °C, (c) 365 °C, (d) 386 °C.



3.5a

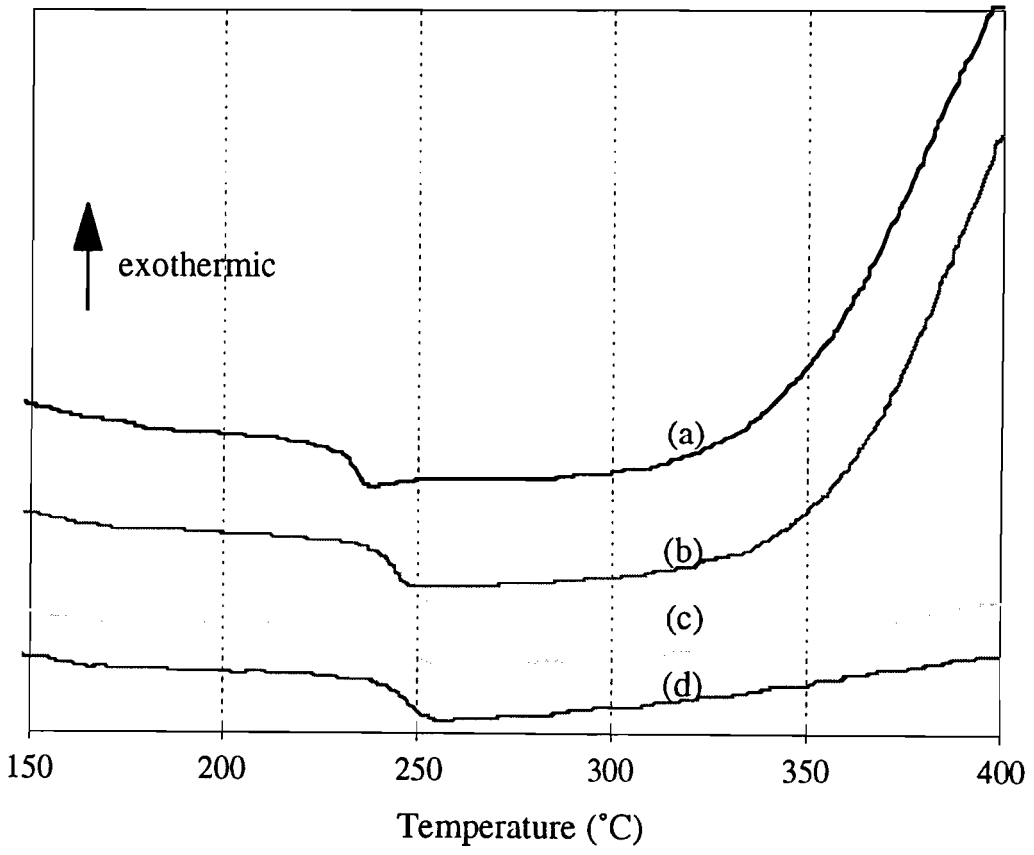
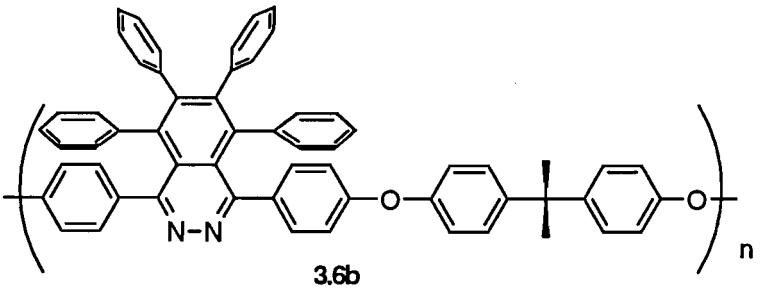
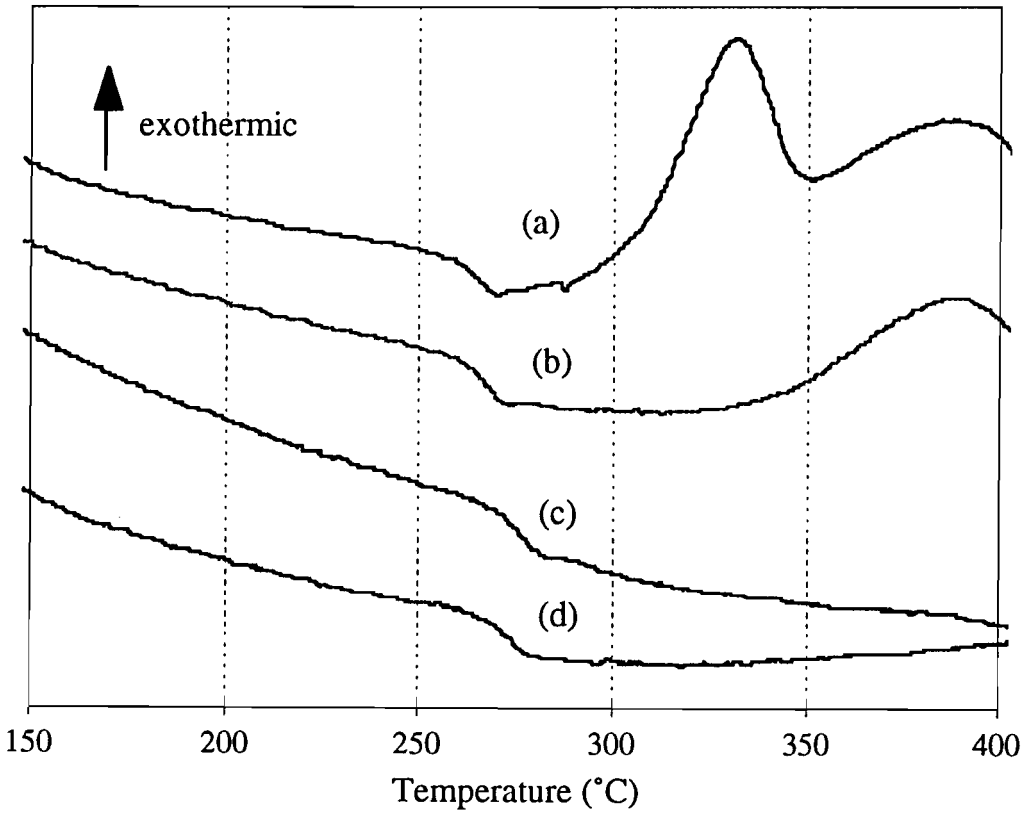


Figure 3.5. DSC traces of polymer **3.6b** after curing at various temperatures for 30 min under nitrogen; (a)260 °C, (b) 310 °C, (c) 355 °C, (d) 399 °C.



3.6b

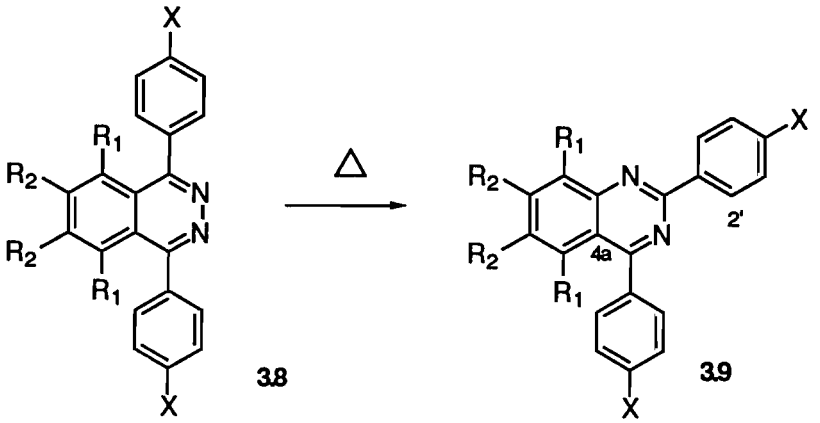


These results suggested that diphenylphthalazine containing polymers **3.4** underwent extensive cross-linking during the exothermic reaction, which indicated that extensive intermolecular reactions take place in these diphenylphthalazine containing polymers when heated. The tetraphenyl and hexaphenyl phthalazine containing polymers **3.5** and **3.6**

underwent only a low degree of cross-linking which suggested that the thermal reaction was mainly intramolecular in polymers **3.5** and **3.6**.

Model compounds study. In order to further understand the molecular basis of the exothermic reaction, a series of polyphenylated phthalazine compounds **3.8** were used as model compounds. When tetraphenylphthalazine **3.8b** was heated in a sealed tube at 360°C for 30 min, a new product was isolated in high yield (70% by weight) and no starting material was recovered.

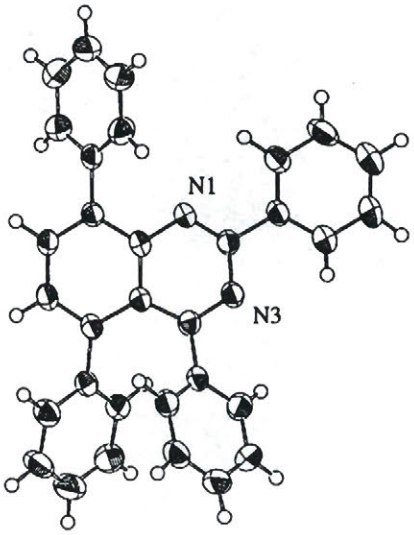
Scheme 3.2



a $R_1 = R_2 = H$, X = F
b R_1 = Ph, R_2 = H, X = H
c $R_1 = R_2$ = Ph, X = H
d $R_1 = R_2$ = Ph, X = F

To our surprise, high resolution MS indicated that this new product has exactly the same mass and molecular formula as the starting material **3.8b**. Extensive, ^1H, ^{13}C and 2D NMR experiments and other analyses were carried out on the product, and based on the spectroscopic data, we assigned the product as tetraphenylquinazoline **3.9b**. In particular, two pieces of evidence are noteworthy; (1) a down field proton signal at 8.6 ppm is very characteristic of a proton-2' of a phenyl attached to the 2-position of a quinazoline; (2) a very up field quaternary carbon signal at 121 ppm is very characteristic of carbon-4a of quinazoline. [2] Since no previous examples of a rearrangement of phthalazine to quinazoline have been reported, X-ray analysis was performed on the product and it confirmed the product is indeed **3.9b** (Figure 3.6).

Figure 3.6. X-ray crystal structure of **3.9b.**



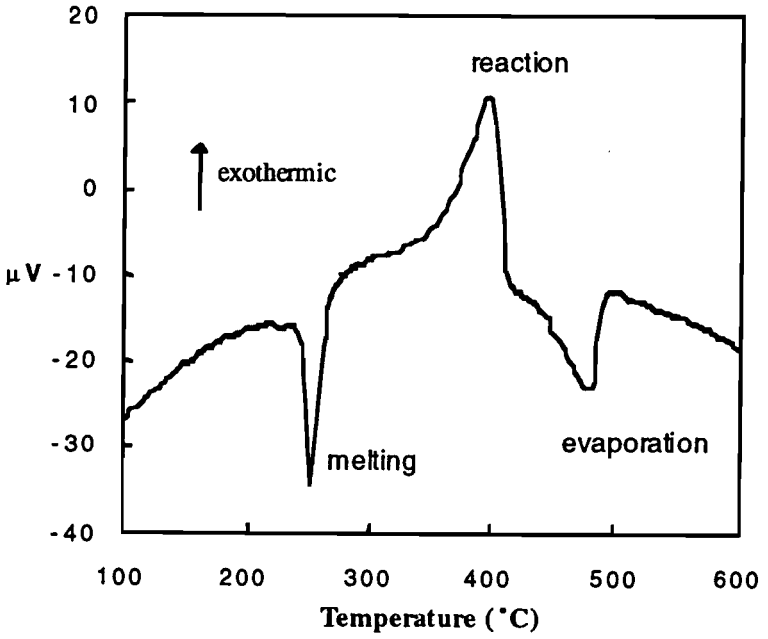
Experiments have also been performed on other model compounds (Table 3.2). Hexaphenylphthalazines **3.8c** and **3.8d** were found to give the cleanest reactions and highest yields of the quinazolines **3.9c** and **3.9d**, respectively. However, in the case of the diphenyl phthalazine **3.8a**, only a low yield of the quinazoline **3.9a** was obtained and decomposition occurred to give principally black, insoluble material.

Table 3.2. Pyrolysis of phthalazines.

Substrate	Product	Temp. °C	Time (h)	Yield/%	Conversion/%
3.8a	**3.9a**	360	14.0	23	30
3.8a	**3.9a**	400	3.5	24	100
3.8b	**3.9b**	360	0.5	70	100
3.8c	**3.9c**	360	0.5	75	100
3.8d	**3.9d**	360	0.5	75	100

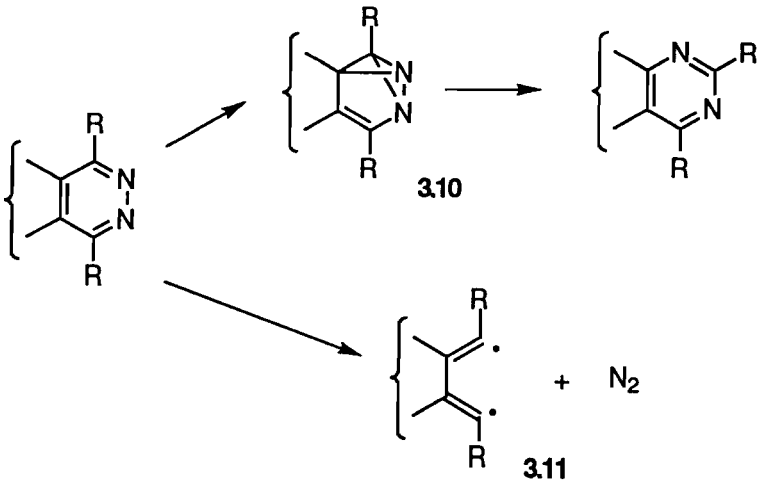
Examination of compound **3.8c** by differential thermal analysis (DTA) (Figure 3.7) and differential scanning calorimetry (DSC) showed that the rearrangement was an exothermic reaction. The enthalpy change of the reaction was found to be 84 kJ/mole and the activation energy was found to be 160 kJ/mole. [3,4]

Figure 3.7. DTA Thermograph of **3.8c.**



A cross-over reaction was carried out using a 1:1 mixture of **3.8c** with **3.8d**. It was found that beside **3.9c**, and **3.9d** no cross-over products were detected. This suggests that the reaction is unimolecular in nature. One of the probable mechanisms for this rearrangement is a unimolecular pathway through a "benzvalene" type intermediate **3.10** as shown in Scheme 3.3 similar to that suggested by Scott for the thermal rearrangement of naphthalene. [5]

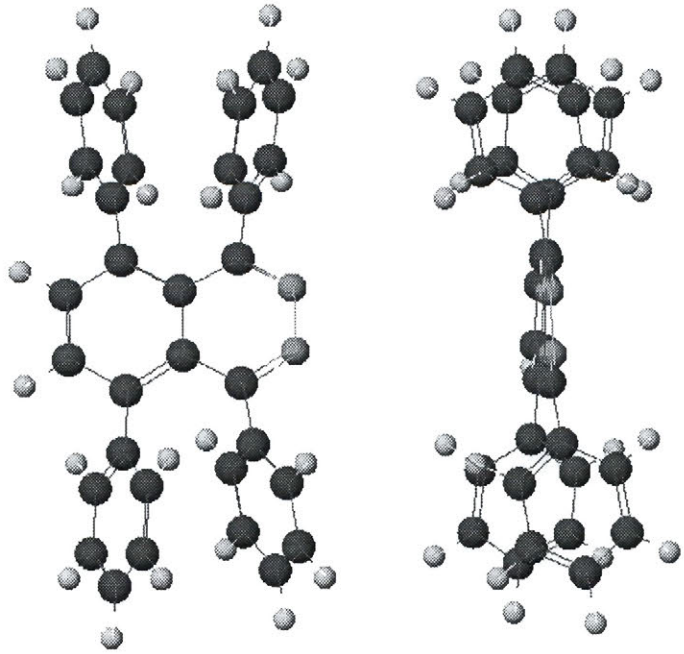
Scheme 3.3



Skeletal rearrangement of aromatic compounds are not commonly observed except at very high temperatures. For example, the thermal automerization of naphthalene was shown to occur only above 1000 °C. [5] In comparison the rearrangement of the phthalazines **3.8b**, **3.8c**, and **3.8d** is extremely facile. This may be attributable to the presence of the heteroatoms which lower the degree of aromaticity in the phthalazine ring compared to naphthalene.

Analysis of molecular model of phthalazine **3.8b** (Figure 3.8) [6] revealed that there is significant repulsion between the phenyl rings in the peri-positions which not only forces the two rings apart but also results in an out of plane splaying of the pendent phenyl rings in opposite directions as occurs in 1,4,5,8-tetraphenylnaphthalene, along with some in plane distortion of the central ring. [7] It appears, therefore, that the presence of this steric repulsion between phenyl rings in the case of **3.8b**, **3.8c**, and **3.8d** is a driving force for the rearrangement, since the relief of steric strain in the juxtaposed phenyl rings could compensate for the loss of aromaticity during the rearrangement process. On the other hand, in the case of **3.8a**, where there is much less steric strain, nitrogen elimination may have occurred preferentially which would lead to decomposition (Scheme 3.3), hence, only a low yield of rearrangement product **3.9a** is obtained.

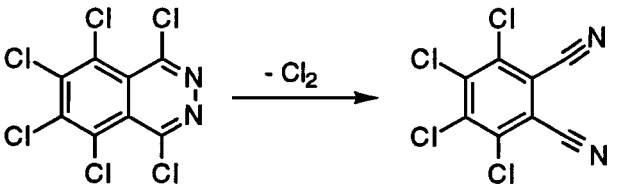
Figure 3.8. Molecular models of 3.8b.



Front View Side View

A MM2 calculation [6] also supports our argument. We have computed the strain energy difference between the phthalazines **3.8a-c** and their corresponding thermal rearrangement products, quinazolines **3.9a-c**. [8] It indeed showed that **3.8b & 3.8c** have higher strain energy (38 kJ/mol) compared to diphenylphthalazine **3.8a** (25 kJ/mol).

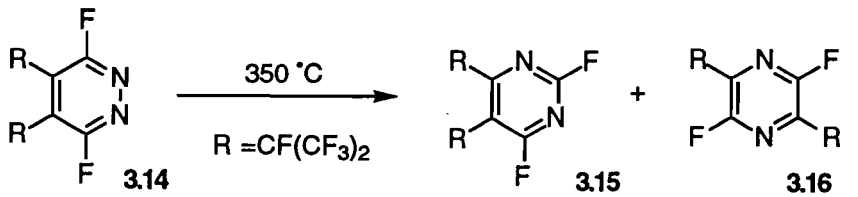
Scheme 3.4



3.12 **3.13**

Nitrogen elimination is reported to be the dominant reaction for phthalazine compounds at elevated temperatures. [9] It has also been reported that pyrolysis of hexachlorophthalazine **3.12** gave the dicyano compound **3.13** (Scheme 3.4). [10] Our results are the first examples of thermal rearrangement of phthalazines to a quinazolines. It also demonstrates once again the role of steric strain in controlling the course of a chemical reaction. [11] The thermal rearrangement of phthalazine to quinazoline exhibits some similarity with the case of perfluoropyridazine **3.14** reported by Chambers et al, which undergo thermal rearrangement to give a mixture of pyrimidine **3.15** and pyrazine **3.16** (Scheme 3.5). [12] However, rearrangement of the perfluoropyridazine **3.14** is governed by electronic factors rather than steric factors and it is much slower compared to our examples.[13]

Scheme 3.5



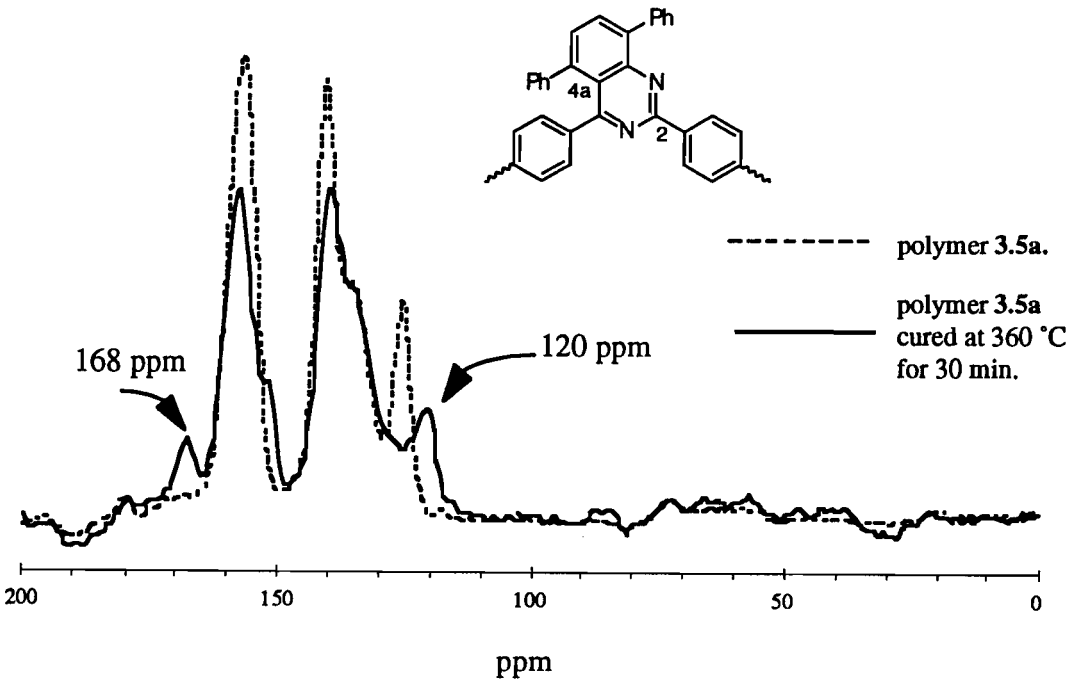
3.14 **3.15** **3.16**

Two possible reaction pathways for the thermal reaction of pyridazines and phthalazines may involve nitrogen elimination through a diradical intermediate **3.11** or rearrangement, probably through a "benzvalene" type intermediate **3.10**. (Scheme 3.3) The competition between rearrangement and elimination of nitrogen depends on a number of factors. The pyridazine **3.14** undergoes rearrangement because the fluorine adjacent to the nitrogen destabilizes the radical intermediate so that the rearrangement reaction is favored over nitrogen elimination. [12] Our case illustrates the importance of steric strain

since the steric crowding effect could decrease the activation energy required for the rearrangement reaction, hence favoring rearrangement over nitrogen elimination.

From the model compound studies, we concluded that polymers containing a tetraphenyl or hexaphenyl phthalazine moiety **3.5** and **3.6** mainly undergo backbone rearrangement reaction, in which the phthalazine moiety rearranges to the corresponding quinazoline moiety. This explains why there is very little increase in Tg and degree of cross-linking in these polymers after thermal treatment. However, diphenylphthalazine containing polymers **3.4** mainly underwent intermolecular coupling reaction which resulted in a highly cross-linked network after thermal treatment.

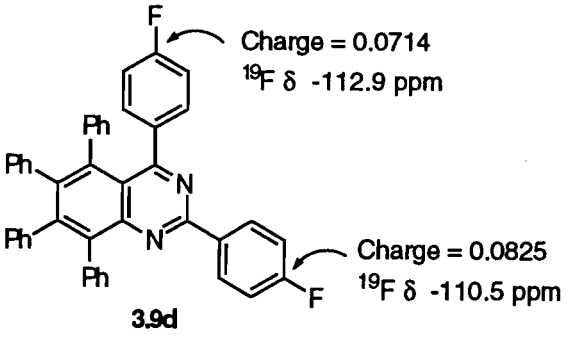
Figure 3.9. Dipolar dephasing magic angle spinning ^{13}C solid state NMR spectra of poly(aryl phthalazine) **3.5a** before and after curing at 360 °C for 30 min under nitrogen atmosphere.



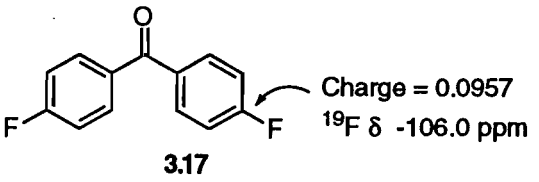
Solid state NMR study. We have obtained the ^{13}C solid state NMR spectra of poly(aryl phthalazine) **3.5a** before and after thermal curing at 360 °C for 30 min. There is no obvious difference in the normal cross polarization-magic angle spinning (CP-MAS) spectra of these samples. However, in the dipolar dephasing spectra, in which only signals of non-protonated carbons were detected, significant difference between the two samples was observed (Figure 3.9). There is a clear indication of a very up field quaternary carbon signal at 120 ppm which is very characteristic for C-4a of a quinazoline

moiety, and a signal at 168 ppm which corresponds to C-2 of a quinazoline moiety. Both of these signals are absent in the original polymer. The result is consistent with the conclusion that the phthalazine moiety of polymer **3.5a** rearranged to a quinazoline.

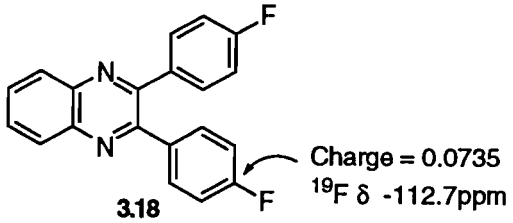
Synthesis of poly(aryl ether quinazoline) polymer. Utilizing this new rearrangement reaction we synthesized in high yield the difluoro-monomer **3.9d**. A number of heterocyclic rings have been shown to act as electron withdrawing groups to activate aromatic dihalides to undergo polycondensation with bisphenols through nucleophilic aromatic substitution. [14] Hence, we were interested to see whether the difluoro quinazoline **3.9d** would be reactive enough to be polymerized with bisphenols. A quantum semiempirical PM3 calculation [15] indicated that this difluoro compound should be reactive toward nucleophilic substitution with a phenoxide since the charges at carbon-4' and 4'', which are *ipso* to the fluorine, were found to be 0.0825e and 0.0714e respectively. These values are higher than that of fluorobenzene (**3.19**), although not as high as that of difluorobenzophenone **3.17**. However, the value is comparable to that of 2,3-bis(4-fluorophenyl)quinoxaline **3.18**, which has been successfully polymerized with bisphenols by a nucleophilic aromatic substitution reaction. [16]



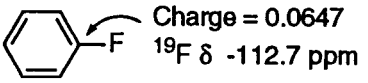
3.9d



3.17



3.18



3.19

We have also use the ^{19}F NMR chemical shifts as a measure of reactivity of **3.9d**.[15a] The ^{19}F chemical shifts of the fluorine on C-4' is found to be -110.5 ppm which indicates a moderate reactivity toward nucleophilic aromatic substitution reaction. However, chemical shift of the fluorine on C-4'' is found to be -112.9 ppm which is only comparable to that of fluorobenzene **3.19**. We attempted to polymerize monomer **3.9d**

with BPA **3.20** by a nucleophilic substitution reaction using DMAc as solvent and potassium carbonate as base, we were able to obtain high molecular weight polymer with M_w = 29 kg/mol and M_n = 13 kg/mol, and an inherent viscosity of 0.3 dL/g. A ^{1}H NMR of polymer **3.21** is shown in Figure 3.10, which is consistent with the structure **3.21**. The polymer has a glass transition temperature of 264 °C, and by thermogravimetric analysis shows a 5% weight loss at 514 °C in nitrogen, which is comparable to its isomeric counterpart, the phthalazine containing polymer **3.6b**.

Scheme 3.6

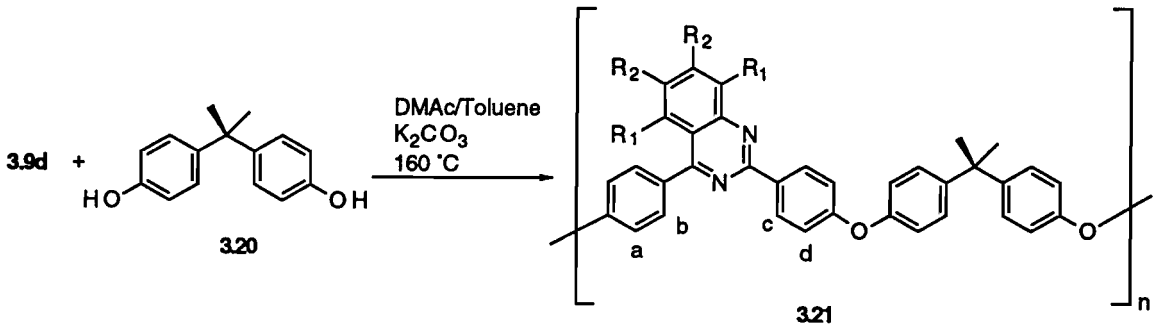
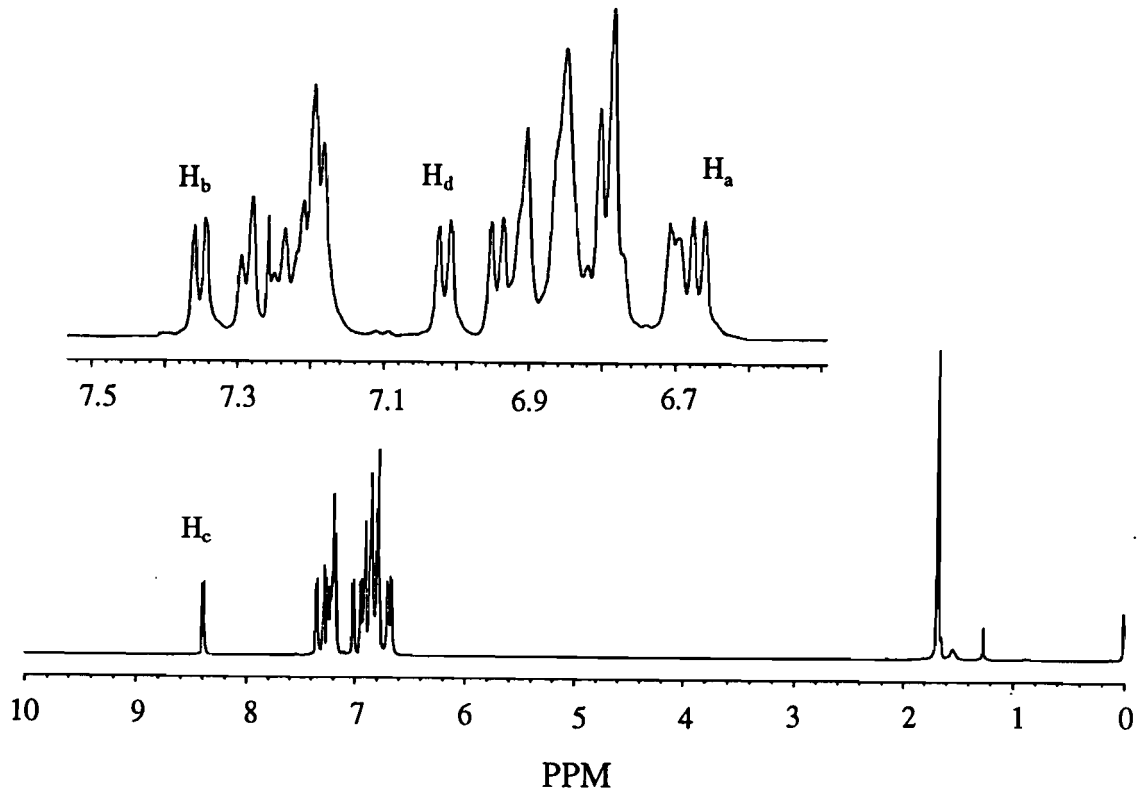
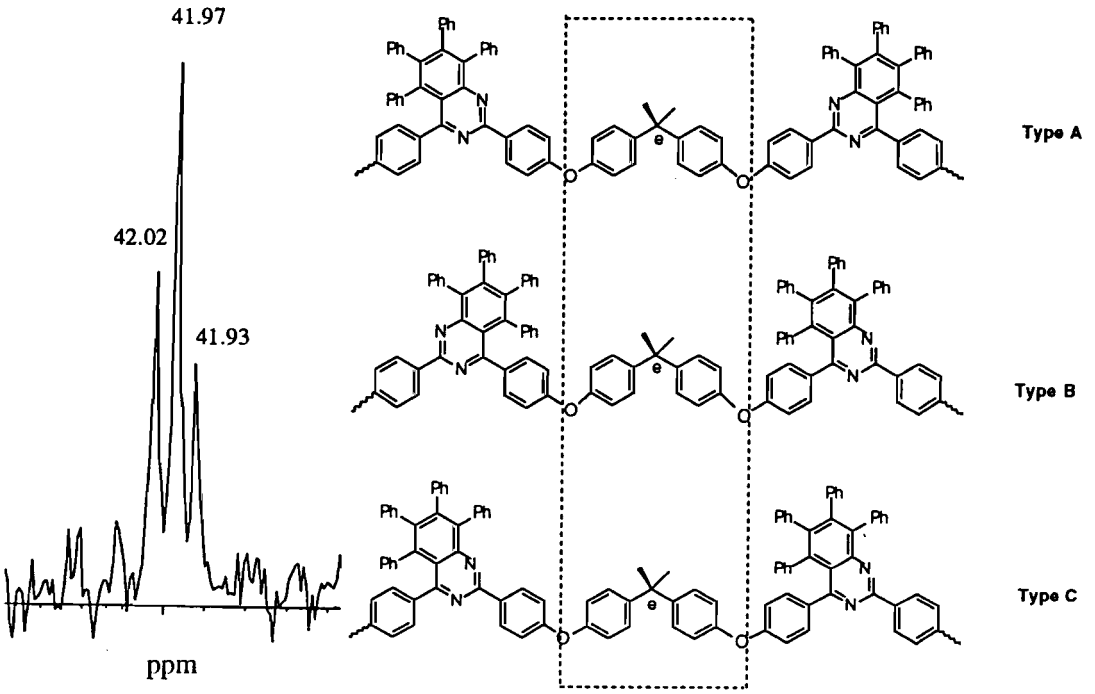


Figure 3.10. ^{1}H NMR (500 MHz,$CDCl_3$) of poly(aryl ether quinazoline) **3.21.**



We were interested to see whether polymer **3.21** has a random or regular polymer sequence. If the difference in reactivity between C-4' and C-4'' of monomer **3.9d** is large enough as indicated by both charge calculation values, and ^{19}F chemical shift measurements, we might obtain a polymer with very regular back bone sequence even though monomer **3.9d** is unsymmetrical. However, the ^{13}C NMR spectra of polymer **3.21** indicated that the polymer had a random sequence. For example, three signals were observed for the quaternary carbon of the isopropylidene group C-e (Figure 3.11), which suggested a random polymer sequence with three type of ether linkages A, B, and C, are all present in the polymer **3.21**. If the polymer indeed had a regular sequence because of the reactivity difference in the two fluorophenyl arms of **3.9d**, only linkages of type A , and B would be formed, which would give only two signals for C-e.

Figure 3.11. ^{13}C NMR (125 MHz,$CDCl_3$) signal of C-e of polymer **3.21.**



3.3 Conclusions

Poly(aryl ether phthalazine)s were found to undergo an exothermic reaction at a temperature range of 360 - 440°C. At elevated temperatures, polymers containing a diphenylphthalazine moiety, **3.4** underwent extensive thermal cross-linking as a result of a

nitrogen elimination reaction of the phthalazine moiety. On the other hand, polymers containing a tetraphenyl of hexaphenyl phthalazine moiety, **3.5** and **3.6**, were found to undergo principally a backbone rearrangement reaction, in which the phthalazine moiety rearranged to a quinazoline. The results are based on thermal analyses, model compound studies, and ^{13}C solid state NMR studies. Utilizing the efficient thermal rearrangement of polyphenylated phthalazines, we have prepared a novel activated difluoride, 2,4-bis(4-fluorophenyl)-,5,6,7,8-tetraphenylquinazoline **3.9d**, which underwent high temperature solution polycondensation with BPA to give quinazoline containing poly(aryl ether) **3.21**. Polymer **3.21** is amorphous, has glass transition temperature of 264 °C and has high thermooxidative stability with 5% weight loss being recorded at 540 °C in nitrogen.

Furthermore, during the model compound studies, we discovered the first thermal rearrangement reaction of a phthalazine to its structural isomer, a quinazoline. We have found that heating polyphenylated phthalazines **3.8b, c, d** at 360 °C for 30 min. gave the corresponding quinazolines in high yield. The less sterically crowded 1,4-bis(4-fluorophenyl)phthalazine **3.8a** gave only a low yield of quinazoline **3.9a**. X-ray crystallographic analysis on **3.9b** further confirmed our finding.

3.4 Experimental

Instrumentation. ^{1}H, ^{13}C, and ^{19}F NMR experiments were recorded at room temperature on a Unity-500 NMR spectrometer. Solid state CP-MAS and DP-MAS ^{13}C NMR experiments were performed on a Chemagnetic CMX-300 spectrometer at 75 MHz with spinning of 5 KHz. EI mass spectra were record on a DuPont 21-492B spectrometer. GPC analyses were performed on a Waters 510 HPLC equipped with phenogel 5μ linear columns (7.8 x 300 mm) with THF as solvent, and a UV detector (254 nm). The molecular weight measurements were obtained by calibration with polystyrene standards. Thermal analyses were obtained by using a Seiko 220 DSC and 220 TGA/DTA instruments with heating rate of 20 °C per min under nitrogen atmosphere.

Solid State NMR spectra of polymers were performed by Dr. Fred Morin at the Department of Chemistry, McGill University.

X-ray crystallography of tetraphenylquinazoline **3.9b** was performed by Dr. A. M. Lebuis at the Department of Chemistry, McGill University.

Polymers **3.4**, **3.5** and **3.6** were obtained according to reported methods. [2]

Synthesis of Phthalazines 3.8a-d. Phthalazines were prepared **3.8a** and **3.8d** by reported method.[1] **3.8b** and **3.8c** were prepared according to the reported procedure [1] using benzene instead of fluorobenzene as starting material. **3.8b** was prepared in 65% yield, mp 342-4 °C (lit. [17] mp 344 °C). **3.8c** was prepared in 80% yield, mp 251-2°C (lit.[18] 249-51 °C).

General Procedure for thermal curing of poly(aryl phthalazine)s. 5 mg of the polymer was cured on a TGA instrument under nitrogen, and the Tg of the cured material was then measured by a DSC instrument under nitrogen atmospohere at a heating rate of 20 °C /min.

General procedure for static thermolysis of phthalazines. Thermolysis was carried out in a sealed tube containing 500 mg of phthalazine using a heated aluminum block according to the temperatures and times reported in Table 3.2. The product was dissolved in chloroform and filtered. Solvent was removed on a rotary evaporator, and the product was purified by column chromatography (silica gel, 10 % EtOAc/ low boiling petroleum ether).

2,4-Bis(4-fluorophenyl)quinazoline 3.9a. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.69 (dd, J=5.9, 8.8 Hz, 2H), 8.12 (d, J=8.3 Hz, 1H), 8.08 (d, J=8.3 Hz, 1H), 7.88 (m, 3H), 7.55 (t, J=7.3 Hz, 1H), 7.29 (dd, J=8.3, 8.3 Hz, 2H), 7.19 (dd, J=8.3, 8.3 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 115.42 (d, J_{CF}=21.9 Hz), 115.67 (d, J_{CF}=21.1 Hz), 121.38, 126.67, 127.13, 129.13, 130.68 (d, J_{CF}=8.2 Hz), 132.13 (d, J_{CF}=9.2 Hz), 133.62 (d, J_{CF}=3.6 Hz), 133.70, 134.20 (d, J_{CF}=2.7 Hz), 151.96, 159.18, 163.94 (d, J_{CF}=250 Hz), 164.63 (d, J_{CF}=250.9 Hz), 167.15; HRMS (EI) *m/e* calcd for $C_{20}H_{12}F_2N_2$: 318.09685, found 318.09690.

2,4,5,8-Tetraphenylquinazoline 3.9b. mp 201-3°C (EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.67 (dd, J=2.0, 8.3 Hz, 2H), 8.04 (d, J=7.3 Hz, 1H), 7.96 (dd, J=1.5, 8.3 Hz, 2H), 7.65 (d, J=7.32 Hz, 1H), 7.62 (dd, J=7.3, 7.3 Hz, 2H), 7.53 (t, J=7.8 Hz, 1H), 7.50 (m, 3H), 7.45 (dd, J=1.5, 8.3 Hz, 2H), 7.05 - 7.15 (m, 8H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 120.21, 126.75, 127.36, 127.39, 127.5, 127.72, 127.85, 128.42, 128.68, 129.66, 130.05, 130.21, 130.43, 131.13, 133.11, 137.87, 138.62, 139.43,

140.23, 140.33, 140.98, 150.89, 158.1, 168.38; HRMS (EI) *m/e* calcd for $C_{32}H_{22}N_2$: 434.17829, found 434.17810.

X-Ray Structure Determination of 3.9b: Crystal dimensions 0.35 x 0.20 x 0.47 mm, measured at 21°C on a Rigaku AFC6S diffractometer with graphite monochromated CuK_α radiation. Monoclinic, a = 19.878(2) Å, b = 16.671(4) Å, c = 14.984(1) Å, β = 69.786(6)°, V = 4660 (2) Å^3, space group $P2_1/c$ (No.14), Z = 4, D_c = 0.619 gcm^{-3}, μ(CuKα)= 2.61 cm^{-1}. $2\theta_{max}$ = 140 °, 4783 reflections which were collected, 4737 were unique of which 2394 observed ($/F_o/ > 3\sigma/F_o/$) and 396 parameters for the refinement with R =0.056 R_w =0.062. Calculations were performed using the Texan crystallographic software package of Molecular Structure Corporation. The structure was solved by direct methods and refined by full matrix least-squares. The non-hydrogen atoms were refined anisotropically.

2,4,5,6,7,8-Hexaphenylquinazoline 3.9c. mp 264-5°C (EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.46 (m, 2H), 7.41 (m, 3H), 7.23 - 7.37 (m, 7H), 7.05 (m, 3H), 6.85 - 6.95 (m, 8H), 6.72 - 6.77 (m, 7H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 121.15, 125.55, 125.86, 126.05, 126.24, 126.57, 126.74, 126.77, 126.84, 127.18, 128.04, 128.31, 128.57, 129.90, 130.26, 130.86, 131.41, 132.03, 132.22, 137.83, 137.98, 138.35, 139.25, 139.27, 139.47, 139.78, 141.04, 141.21, 146.02, 151.01, 157.92, 169.06; HRMS (EI) *m/e* calcd for $C_{44}H_{30}N_2$: 586.24090, found 586.24140.

2,4-Bis(4-fluorophenyl)-5,6,7,8-tetraphenylquinazoline 3.9d. mp 255-6°C (EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.40 (dd, J=6.0, 9.5 Hz, 2H), 7.22 - 7.36 (m, 7H), 7.09 (dd, J=9.5, 9.5 Hz, 2H), 6.96 (m, 3H), 6.88 (m, 5H), 6.7 - 6.84 (m, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 114.18 (d, J_{CF}=22.0 Hz), 115.29 (d, J_{CF}=22.0 Hz), 120.96, 125.66, 125.94, 126.24, 126.33, 126.64, 126.81, 126.89, 126.92, 130.59 (d, J_{CF}=8.2 Hz), 130.79, 131.37, 131.74 (d, J_{CF}=8.2 Hz), 131.93, 132.17, 133.92 (d, J_{CF}=2.7 Hz), 137.02 (d, J_{CF}=3.7 Hz), 137.88, 138.16, 139.13, 139.29, 139.62, 141.41, 146.32, 151.07, 157.03, 162.43 (d, J_{CF}=248.2 Hz), 164.48 (d, J_{CF}=250.0 Hz), 168.00; HRMS (EI) *m/e* calcd for $C_{44}H_{28}F_2N_2$: 622.2204, found 622.2217; Analysis calcd for $C_{44}H_{28}F_2N_2$: C, 84.87; H, 4.53; N, 4.50; found: C, 84.99; H, 4.64; N, 4.46.

Poly[2,4-(5,6,7,8-tetraphenylquinazolinylene) -1,4-phenyleneoxy-1,4-phenylene-isopropylidene-1,4-phenyleneoxy-1,4-phenylene] 3.21. The polymerization was conducted in a 25 mL three-neck round bottom flask which was equipped with a nitrogen inlet, thermometer, Dean-Stark trap, and condenser. The flask was charged with 2,4-bis(4-fluorophenyl)-5,6,7,8-tetraphenylquinazoline **3.9d** (1g, 1.6 mmol), 4,4'-isopropylidenediphenol **3.20** (366 mg, 1.6 mmol), DMAc (12 mL), toluene (5 mL), and potassium carbonate (440 mg). The solution was magnetically stirred and heated to reflux. The temperature range of the solution was kept at 120-30 °C for 4 h. Solution temperature was then increased to 160 °C by removal of toluene from the Dean-Stark trap. The resulting solution was refluxed for another 16 h. The reaction mixture was cooled and precipitated into methanol. The residue was dissolved in 20 mL of hot chloroform and filtered through a layer of celite. The chloroform solution was concentrated to 4 mL and precipitated into methanol. The precipitate was filtered, and dried in a vacuum oven (120 °C) for 12h to give the desired polymer **3.21** (75% yield, 1g). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.38 (d, J = 8.8 Hz, 2H),7.34 (d, J = 8.8 Hz, 2H),7.14 - 7.30 (m, 10H), 7.00 (d, J = 8.8 Hz, 2H), 6.74 - 6.95 (m, 16H), 6.68 (m, 2H), 6.65 (d, J = 8.8 Hz, 2H), 1.67 (s, 6H). Mw = 29 kg/mol, Mn = 13 kg/mol. Inherent viscosity = 0.3 dL/g ($CHCl_3$, conc = 0.5 g/dL, 25 °C).

3.5 References and notes

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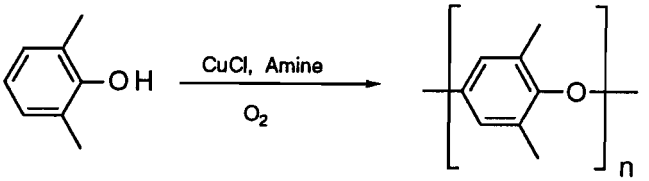
Chapter 4

A Facile Qualitative and Quantitative Analysis of Hydroxy Groups of Poly[oxy-1,4-(2,6-dimethylphenylene)] by ^{31}P NMR Spectroscopy

4.1 Introduction

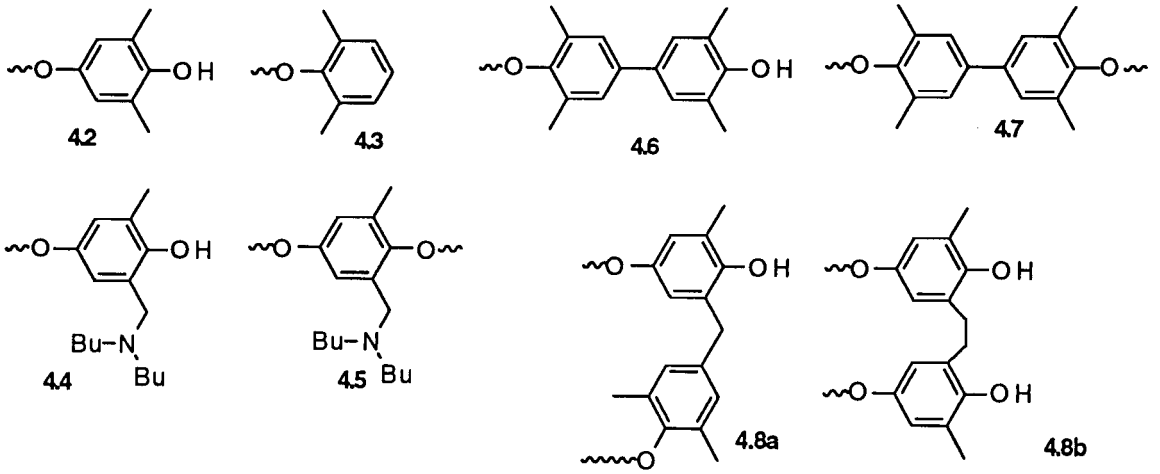
Poly[oxy-1,4-(2,6-dimethylphenylene)], PPO® resin, is an important engineering thermoplastics due to its high Tg, tensile strength, stiffness, impact strength and creep resistance.[1] Noryl® resin, which is a blend of PPO® and polystyrene, is one of the top five major engineering thermoplastic manufactured today. PPO® is usually prepared by oxidative coupling polymerization of 2,6-dimethylphenol in the presence of an amine complexed copper (I) catalyst and oxygen at ambient temperature (Scheme 4.1).[2]

Scheme 4.1



4.1

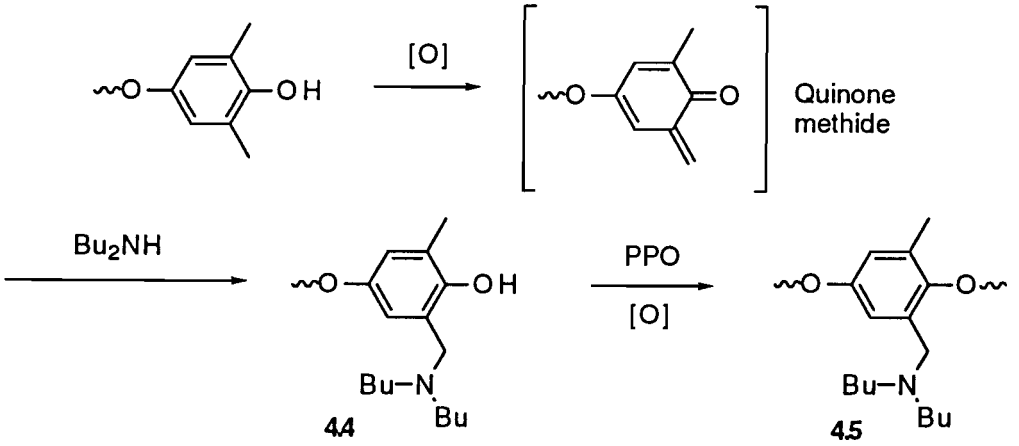
The structure of a PPO® polymer chain in general can be represented by repeating unit **4.1**, and end groups **4.2** & **4.3.** However, recent studies showed that there were a number of other structural units such as **4.4** - **4.8b**, were found to be present in the commercial PPO® resins in minute quantities.



4.2 4.3 4.6 4.7 4.4 4.5 4.8a 4.8b

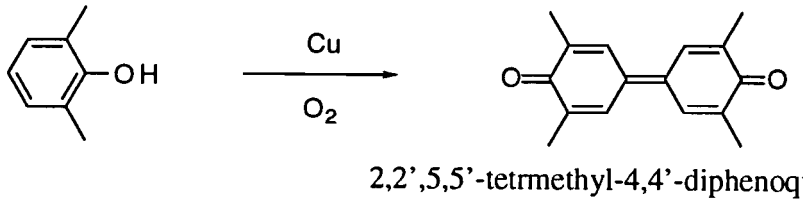
The formation of dibutylaminomethyl units **4.4** and **4.5** are the result of amine incorporation into polymer chain through a quinone methide intermediate (Scheme 4.2). This happens at the later stages of the polymerization when oxidation of the radical by the catalyst can compete with radical coupling reactions. [3]

Scheme 4.2

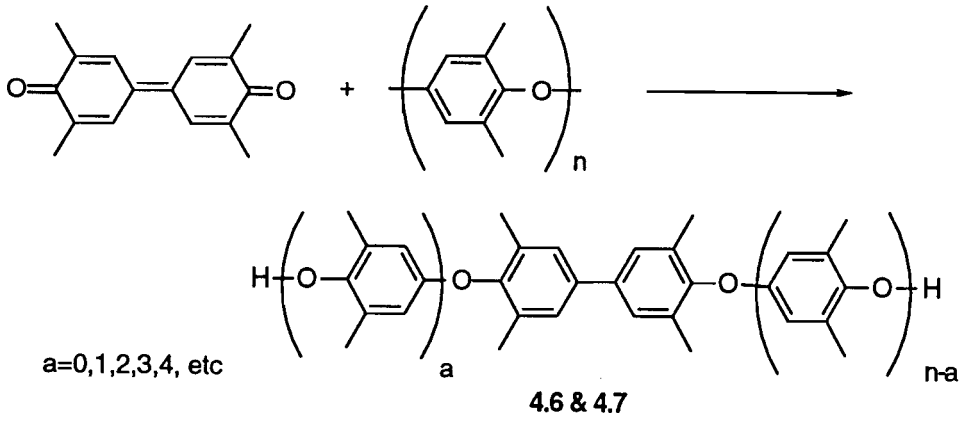


The biphenyl units **4.6** and **4.7** are formed as result of the reaction between 2,2',5,5'-tetramethyl-4,4'-diphenoquinone and PPO® during the polymerization. 2,2',5,5'-Tetramethyl-4,4'-diphenoquinone was a side product of the polymerization of 2,6-dimethylphenol (Scheme 4.3). [4]

Scheme 4.3



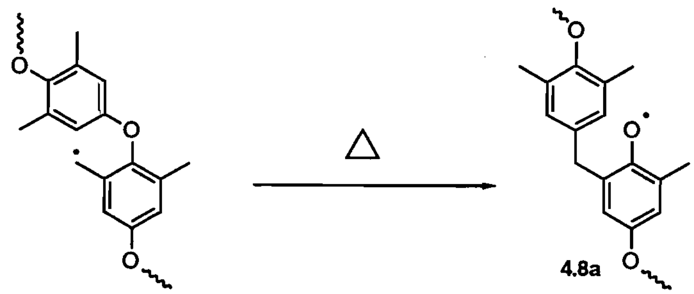
2,2',5,5'-tetrmethyl-4,4'-diphenoquinone



4.6 & 4.7

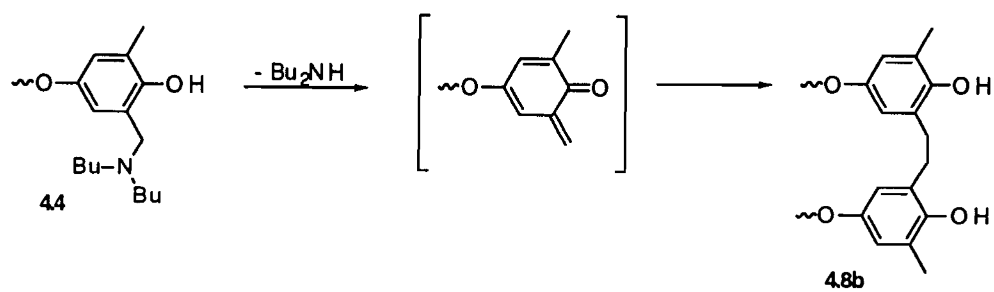
Structural unit **4.8a** is usually found in extruded PPO® resin. It is formed as a result of radical initiated intramolecular backbone rearrangement of PPO® at elevated temperature (350 °C) when PPO® is being extruded (Scheme 4.4).[5,6]

Scheme 4.4



The amount of these structural units present in the resin varies and it depends on the synthetic and the processing conditions employed. Furthermore, these functionalities also greatly influence the ultimate properties of the resin. For example, the terminal dibutylaminomethyl units **4.4** are believed to be responsible for the strong fishy smell observed when PPO® is extruded and also for the viscosity increase of the extruded PPO® resin. Terminal dibutylaminomethyl unit **4.4** presumably undergoes decomposition to give dibutylamine, together with the formation of reactive quinone methide polymer chain ends, which will undergo coupling reaction readily to cause the increase in molecular weight and hence increase in viscosity of the extruded PPO® resin. One of the most probable coupling products is the backbone phenolic unit **4.8b** (Scheme 4.5).

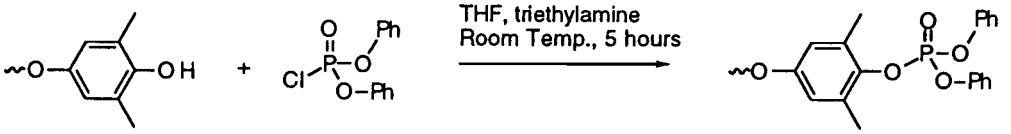
Scheme 4.5



Hence, it would be desirable to have an analytical method that can determine these structural units in PPO® resin both qualitatively and quantitatively. ^{13}C NMR has been proven to be very useful in identifying repeat unit **4.1**, end groups **4.2** & **4.3**, and units **4.4**, **4.5**, **4.6**, **4.7**, **4.8a** and **4.8b** in the polymer.[3-6] However, due to the insensitivity of the ^{13}C nucleus for NMR studies and the low concentration of most of these units, it is still impractical to use it as a routine and reliable analytical tool to determine the concentration of these units.

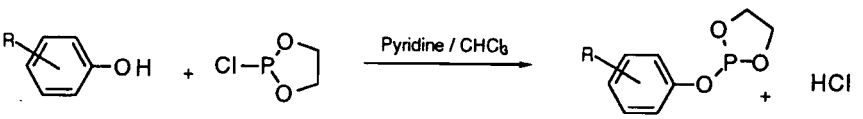
Since most of the trace units in PPO® resin contain labile phenolic hydroxy groups, it was thought that these hydroxy groups could serve as a handle for attaching a more sensitive NMR nucleus which would give stronger and well separated signals for the different structural units. One particular nucleus that we were interested in is phosphorus-31, because it is 377 times more sensitive than carbon. [7] Furthermore, phosphorus has a large range of chemical shift, ~700 ppm, which ensures a good separation of signals of the ^{31}P nuclei in different environments. In addition, it is well known that derivatization of a phenolic group with phosphorus halide is quantitative and fast, and this is very important for ensuring reliable quantitative results. Finally there are no phosphorus atoms in the PPO® resin to cause interference which would make analysis of spectra much easier. Diphenyl chlorophosphate has been used previously to derivatize PPO® hydroxyl groups, and some discrimination of various hydroxyls is achieved by ^{31}P NMR (Scheme 4.6). However, the esterification in this case is relatively difficult and these reactions had to be performed on a large scale, with long reaction times and they required subsequent isolation of the products and introduction of a sample of the derivatized material into the NMR tube for analysis. [8]

Scheme 4.6



In the earlier work by Bolker et al, they found that phenolic compounds derivatized with 1,3,2-dioxaphospholanyl chloride **4.9** can be discriminated nicely by ^{31}P NMR spectroscopy (Scheme 4.7). [9] Furthermore, the derivatization can be easily done directly in a NMR tube. We report here the development of a facile qualitative and quantitative method for the determination of phenolic functional groups in PPO® resin by first derivatizing them with the chloride **4.9** to give a phosphite ester followed by analysis of the derivatized material by ^{31}P NMR spectroscopy.

Scheme 4.7

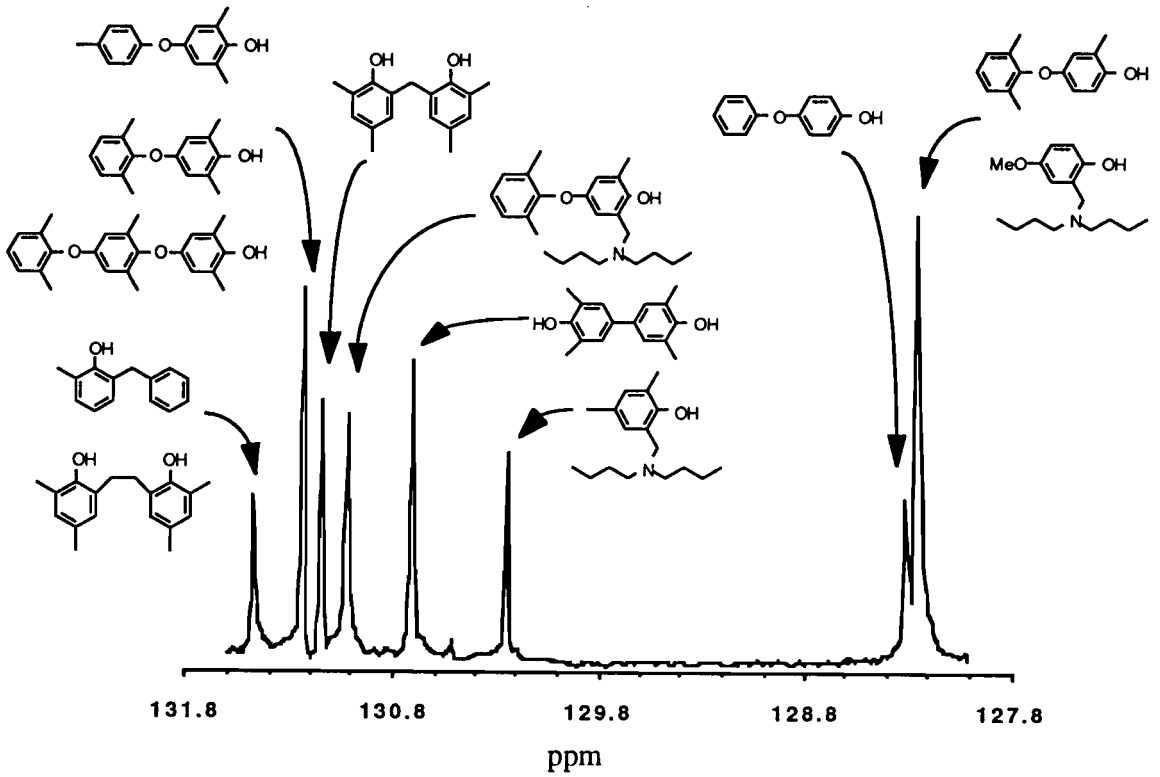


4.9

4.2 Results and discussion

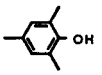
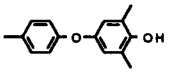
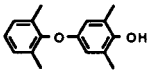
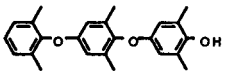
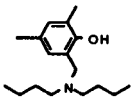
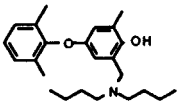
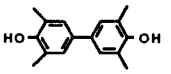
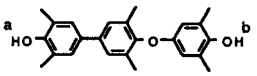
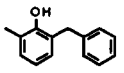
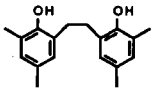
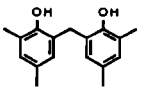
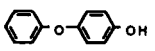
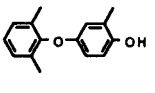
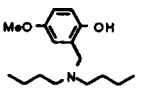
Model compound study. In order to assign the signals that will appear in the spectra of derivatized PPO® resin a number of model compounds have been selected and derivatized with the chloride **4.9**, and their ^{31}P chemical shifts were determined (Table 4.1). Compounds **4.10a** to **4.10d** are models for the normal phenolic end **4.2** of PPO®. Compounds **4.11a** and **4.11b** are models for the dibutylaminomethyl phenolic end **4.4**. Compounds **4.12** and **4.13** are models for the biphenyl phenolic end **4.6**. Compounds **4.14**, **4.15**, and **4.16** are models for backbone phenolic group **4.8a** & **4.8b**. Compounds **4.17**, **4.18** and **4.19** are used to model unhindered phenolic ends that might appear in the PPO® resin.

Figure 4.1. ^{31}P NMR spectrum of phenols derivatized with chloride **4.9**.

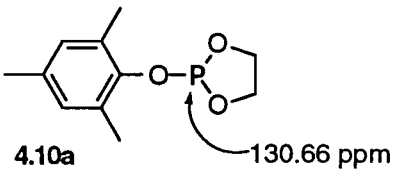


The ^{31}P chemical shifts of different types of phenolic end models were well separated from one another (Figure 4.1), with the exception that the unhindered phenolic end models compounds **4.17**, **4.18** and **4.19** all appeared at 128.2 ppm, and were not well resolved. All 2,6-disubstituted phenolic model compounds gave well separated signals in the region of 130 ppm to 132 ppm (Figure 4.1).

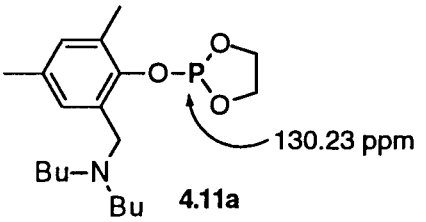
Table 4.1. ^{31}P Chemical shifts of phenols derivatized with chloride **4.9**.

Phenol		Chemical Shift (PPM)
	4.10a	130.66
	4.10b	131.23
	4.10c	131.24
	4.10d	131.21
	4.11a	130.23
	4.11b	131.00
	4.12	130.72
	4.13	[a] 130.72 / [b] 131.26
	4.14	131.47
	4.15	131.50
	4.16	131.18
	4.17	128.30
	4.18	128.24
	4.19	128.24

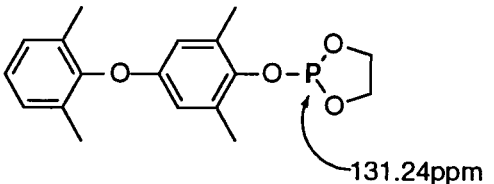
One interesting observation is that within the same type of model compound, those with a phenoxy group at the *para*-position with respect to the phenolic group have a higher chemical shift (~0.5 ppm) than those without (e.g. compare **4.10b**, **c**, **d** to **4.10a**, or **4.11b** to **4.11a**). This is probably due to the electron donating nature of the phenoxy group which increases the induced ring current of the phenyl ring and hence results in a stronger deshielding effect upon the phosphorus nucleus.



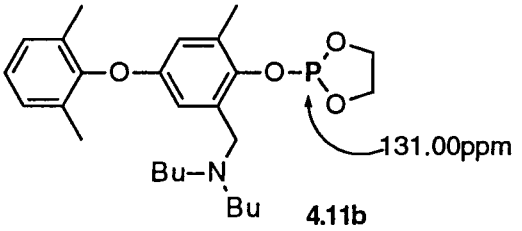
4.10a



4.11a



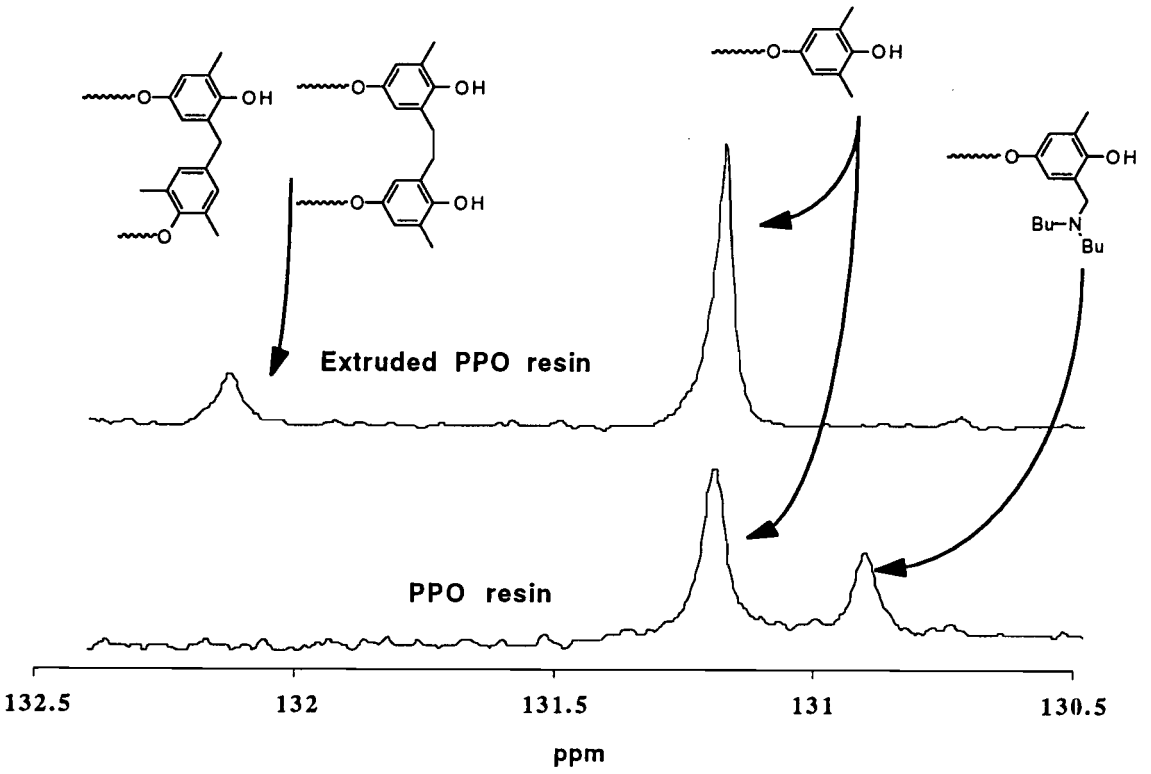
4.10c



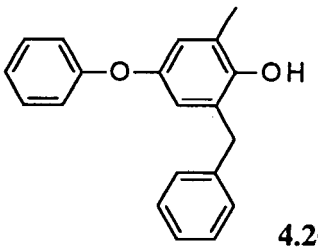
4.11b

PPO® resin samples. Two types of PPO® resins have been investigated. The ^{31}P NMR spectra of PPO® polymers derivatized with chloride **4.9** were obtained with continuous proton decoupling, 45° pulse, acquisition time of 0.5s, and without any delay time for 1 h on a Varian XL300 machine. The first sample is a PPO® resin as isolated and two signals were identified at 131.0 and 131.2 ppm. The second one is an extruded PPO® resin (extrusion temperature was 300 °C), and two signals were identified at 131.2 and 132.1 ppm. By comparing the chemical shift of these signals with that of model compounds, it is obvious that both samples have one common signal at 131.2 ppm which strongly indicates the presence of a normal phenolic end **4.2** in the polymer. The signal at 131.0 ppm in the first sample indicated the presence of the dibutylaminomethyl phenolic end **4.4** in the polymer. Finally, the signal at 132.1 ppm of the extruded PPO® resin may indicate the presence of the backbone phenolic groups **4.8a** or **4.8b** (Figure 4.2). Even though we do not have good models, i.e. **4.20** and **4.21**, for these kind of structures, instead we only have models **4.14** and **4.15**, which give ^{31}P chemical shift of 131.5 ppm upon derivatization (Table 4.1).

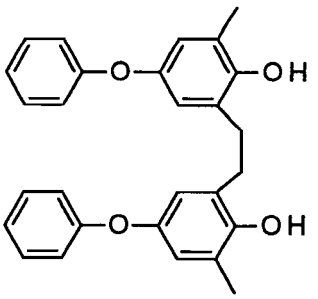
Figure 4.2. ^{31}P NMR spectra of PPO® resins derivatized with chloride **4.9**.



However, as we have already mentioned adding a phenoxy group on the *para*-position of a model compound increases the ^{31}P chemical shift by 0.5 ppm. Therefore, based on logical induction ^{31}P NMR of derivatized model **4.20** and **4.21**, which are different from **4.14** and **4.15** by an *para*-phenoxy group, will have chemical shifts at ~132 ppm.



4.20

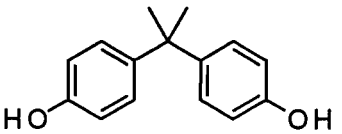


4.21

Therefore, there were only three major signals found in PPO® samples. Other minor signals have also been observed (especially when the acquisition time was prolonged) which may indicate the presence of other phenolic ends in the polymer but present in a

much lower concentration. More effort will be needed to increase the detection limits so that other possible phenolic ends can be identified and quantified.

Quantitative analysis of PPO® and its blends. The use of FT NMR methods of analysis are showing considerable promise with regard to their reliability as analytical tools. The integration of the NMR signal is proportional to the concentration of the nucleus if appropriate experimental conditions are observed. [10]



BPA

In order to measure the amount of each phenolic group present in the PPO® resin by ^{31}P NMR, a suitable compound for use as internal standard was required. By introducing a known amount of standard to a known amount of PPO® resin, the concentration of phenolic ends can be calculated based on the integration ratio of sample and internal standard signal. Bisphenol A (BPA) was found to be a suitable internal standard in our study.

BPA derivatized with chloride **4.9** gave a ^{31}P signal at 128.3 ppm, a region that doesn't overlap with any major signals that we are interested in. It also has a spin-lattice relaxation time T_1 of 7s (at 121.5 MHz). On the other hand, phosphorus nuclei attached to the polymer have a relaxation time less than one second. In order to obtain valid analytical results (10% error), 1.3 times the largest T_1 between successive 45° pulses must be employed [11], therefore a delay of 10s was employed. Intensity distortion due to proton to phosphorus Nuclear Overhauser effect and proton-phosphorus scalar coupling can be eliminated by employing an inverse gated proton decoupling sequence during the acquisition. [12]

A series of quantitative analyses were carried out on three different samples which can be identified as follow: (A) PPO® resin, (B) PPO® and polystyrene alloy blend (1:1 w/w) (PPO/PS), (C) PPO® and high impact polystyrene alloy blend (1:1 w/w) (PPO/HIPS). Results are summarized in Table 4.2.

Table 4.2. Results of ^{31}P analysis of three PPO® resins using chloride **4.9** as derivatizing reagent.

	(A) PPO resin	(B) PPO/PS	(C) PPO/HIPS
(1) Wt % of OH on normal phenolic end **4.2**	0.087	0.045	0.042
(2) Wt % of OH of phenolic end **4.4**	0.039	not detected	not detected
(3) Wt % of OH on backbone phenolic groups	not detected	0.011	0.010
(4) Wt % of total OH groups	0.126	0.056	0.052
(5) Wt % N on phenolic end	0.034	not detected	not detected
(6) M_n ($gmol^{-1}$)	13,400	18,700	20,200

(a) All the percentage values are w/w.

(b) M_n of the PPO® in blend is based on the % weight of PPO®.

Table 4.3. Results of traditional analysis of the three PPO® resins.

	(A) PPO resin	(B) PPO/PS	(C) PPO/HIPS
(1) Wt % of OH [a]	0.090	0.055	0.051
(2) Wt % of N[b]	0.106	0.062	0.051
(3) M_n ($gmol^{-1}$)[c]	12,500	21,200	23,600
(4) M_w ($gmol^{-1}$)[c]	48,000	74,100	72,800

(a) % of OH was determined by FT-IR technique.

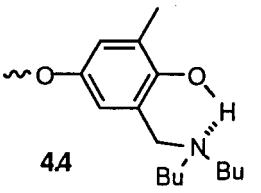
(b) % of N was determined by automated Dumas method using a Carlo Erba NA1500 Nitrogen Analyzer.[13]

(c) Molecular weight was determined using a Waters GPC with 4 Microstyrogel Columns (10^5, 10^4, 10^3, 500 Å) attached to a UV detector with polystyrene standards.

Based on our technique, we are able to obtain the hydroxy concentration of normal phenolic ends **4.2**, phenolic ends **4.4**, and phenolic groups on the backbone **4.8a** or **4.8b** as well as the number average molecular weight of the polymer. In addition the nitrogen content in the phenolic end **4.4** can also be calculated. The analysis was repeated three times for each sample, therefore the precision of the method was determined to be ±0.0015% or ± 15 ppm in the determination of the hydroxy functionality. These results were compared with those obtained from traditional analysis methods (Table 4.3).

It was encouraging to find that the OH content determined by the ^{31}P NMR method was close to that obtained by the infrared method. One limitation of the infrared method is that only hydrogen bonding free phenolic groups are detected. Dibutylaminomethyl

phenolic ends **4.4** are not detected, because of intramolecular hydrogen bonding between the nitrogen and the phenolic group. However our technique can detect all of them. For example, in the case of the first sample of PPO® resin, the total wt % of OH determined by our method was 0.126%, while it was 0.090% by the IR method which is the same value as normal phenolic end (0.087%) determined by the ^{31}P NMR method. In terms of determination of percentage of nitrogen in the polymer, the Dumas method [19] determined the total nitrogen content of the polymer, while the ^{31}P NMR method can determine selectively those nitrogens that appeared in the dibutylaminomethyl phenolic ends **4.4** of the polymer. With the combination of these two results, one can have a better analysis of the distribution nitrogen within the polymer.



4.4 Intramolecular hydrogen bonded structure

4.3 Conclusions

A facile technique has been developed to end cap the phenolic hydroxy groups present in PPO® resin or its blends with a phosphite group, where quantitative derivatization was simply done in the NMR tube in a short time (1/2 h). The ^{31}P NMR spectra of the derivatized PPO® sample gave well separated signals allowing the detection and quantification of normal phenolic ends, dibutylaminomethyl phenolic ends, and backbone phenolic groups in the polymer. The assignment of these signals was based on a model compound study.

Quantitative analysis of these phenolic groups on three different types of PPO® and PPO® blends was achieved with high precision by the application of appropriate NMR acquisition parameters. Hydroxy content as low as 100 ppm can be detected by our method at this stage.

4.4 Experimental

Chemicals. Model compounds and PPO® resins were kindly supplied by General Electric Co. 1,3,2-dioxaphospholanyl chloride **4.9** was obtined from Fluka Chemical Co.

Derivatization Procedure. The model compounds or polymer samples (20 mg) were derivatized in a 5 mm NMR tube with 1:1 mixture of $CDCl_3$ and pyridine as solvent, followed by 20 μL of chloride **4.9**. For quantitative analysis of polymer samples, a typical sample preparation and derivatization was carried out as follows: 600 mg of PPO® sample was first dissolved in 5 mL of $CDCl_3$ in a 10 mL volumetric flask, followed by 1 mL of pyridine solution of bisphenol A (4.06 mg/mL), and the solution was made up to 10 mL using pyridine. 400 μL of the of the above solution was transferred to a 5 mm NMR tube followed by the addition of 30 μL of chloride **4.9**. The resulting solution was shaken for 30 min at room temperature prior to analysis.

NMR spectroscopy. ^{31}P NMR Spectra were measured on Varian XL-200 and XL-300 spectrometers by using a 5 mm broad band probe at 20 °C. The internal lock was provided by $CDCl_3$. All the signals were referenced to the product of chloride **4.9** with water, which chemical shift was set at 121.1 ppm.[9a] For quantitative analysis, the spectra were acquired on a XL300 machine for 5 h with inverse gated proton decoupling sequence, spectral window from 125 to 140 ppm, pulse angle of 45 °, acquisition time of 1 s, and pulse delay of 10 sec. Peak integration was used for the calculation.

Calculation. The weight percentages (wt%) of the hydroxy groups in the PPO® samples were calculated according to peak integration ratio of the phenolic group signal concerned with respected to that of derivatized BPA. Therefore;

(1) Weight percentage of OH on a particular phenolic group = (R x $2M$ x 17x100%)/Wp. Wp is weight of polymer sample, M is number of mole BPA in the polymer sample, and R is the ratio of intensity of the particular derivatized phenolic group signal w.r.t. the BPA signal in ^{31}P NMR.

(2) Wt % N on phenolic end = (wt% of OH on dibutylaminomethyl phenolic end)x14 / 17.

(3) Number average molecular weight M_n;

M_n = 17 / (wt% of OH on normal phenolic and dibutylaminomethyl phenolic end)

The measurements for each polymer sample were repeated three times and average of wt% of hydroxy end were obtained. The uncertainty of the average is calculated from the standard deviation. The measurements and calculations for the wt % results in Table 4.2 are listed in the following Tables.

Table 4.4. Wt % measurements and calculations for (A) PPO® sample.

Weight percentage x10^3

Sample no.	*1*	*2*	*3*	*Average*
OH on normal phenolic end **4.2**	85.7	86.8	89.2	87 ± 2
OH on phenolic end **4.4**	37.3	40.5	41.1	39 ± 2
OH on backbone phenolic groups	0	0	0	0
Total OH groups	122.9	127.3	130.3	126 ± 2

Table 4.5. Wt % measurements and calculations for (B) PPO/PS sample.

Weight percentage x10^3

Sample no.	*1*	*2*	*3*	*Average*
OH on normal phenolic end **4.2**	52.4	44.6	46.2	45 ± 1
OH on phenolic end **4.4**	0	0	0	0
OH on backbone phenolic groups	11.2	11.7	9.4	11 ± 2
Total OH groups	63.6	56.4	55.6	56 ± 2

Table 4.6. Wt % measurements and calculations for (C) PPO/HIPS sample.

Weight percentage x 10^3

Sample no.	*1*	*2*	*3*	*Average*
OH on normal phenolic end **4.2**	41.6	43.2	41.4	42 ± 1
OH on phenolic end **4.4**	0	0	0	0
OH on backbone phenolic groups	9.1	11.1	8.9	10 ± 1
Total OH groups	50.7	54.3	50.3	52 ± 1

4.5 References and notes

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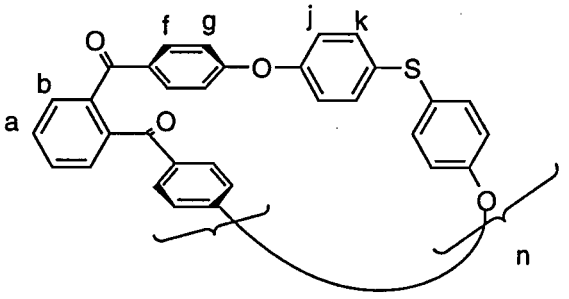
^{1}H NMR (500 MHz, $CDCl_3$) of (i) cyclic oligomer 2.8b, and (ii) its dimer 2.8b(n=2).



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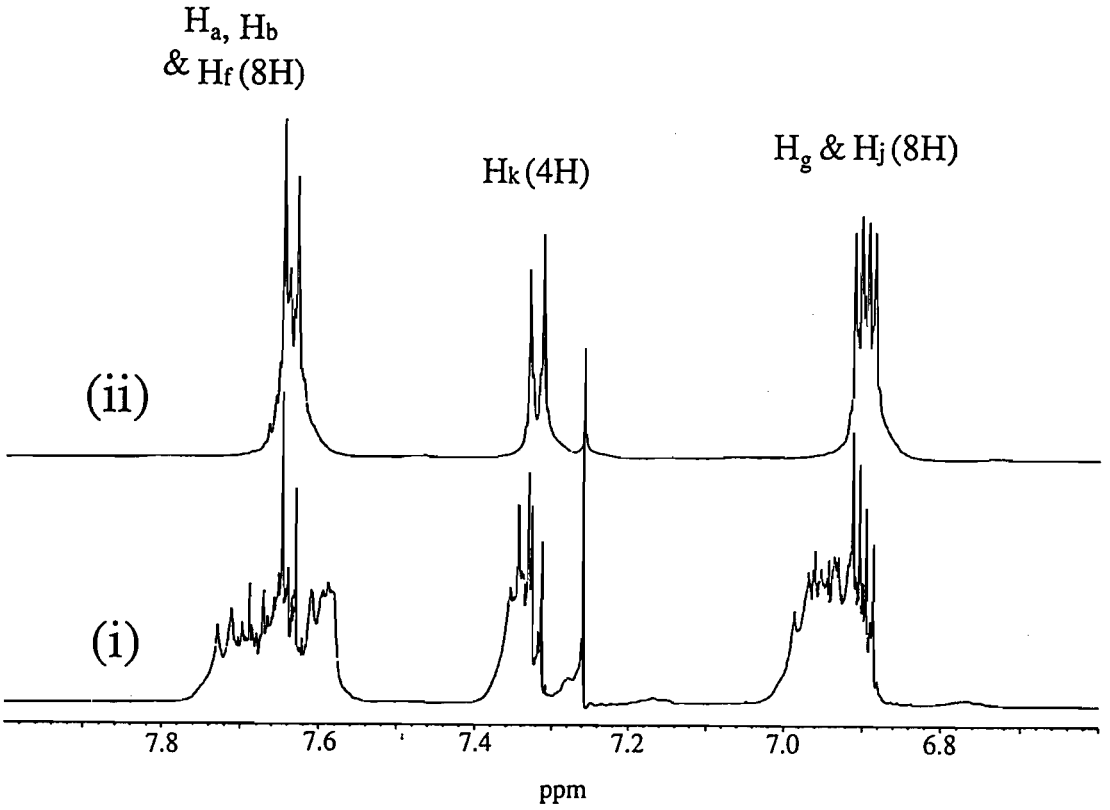
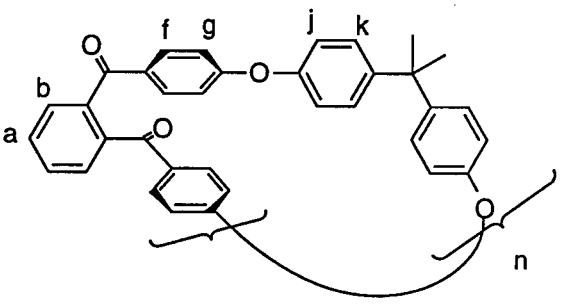


^{1}H NMR (500 MHz, $CDCl_3$) of cyclic oligomer 2.8c.



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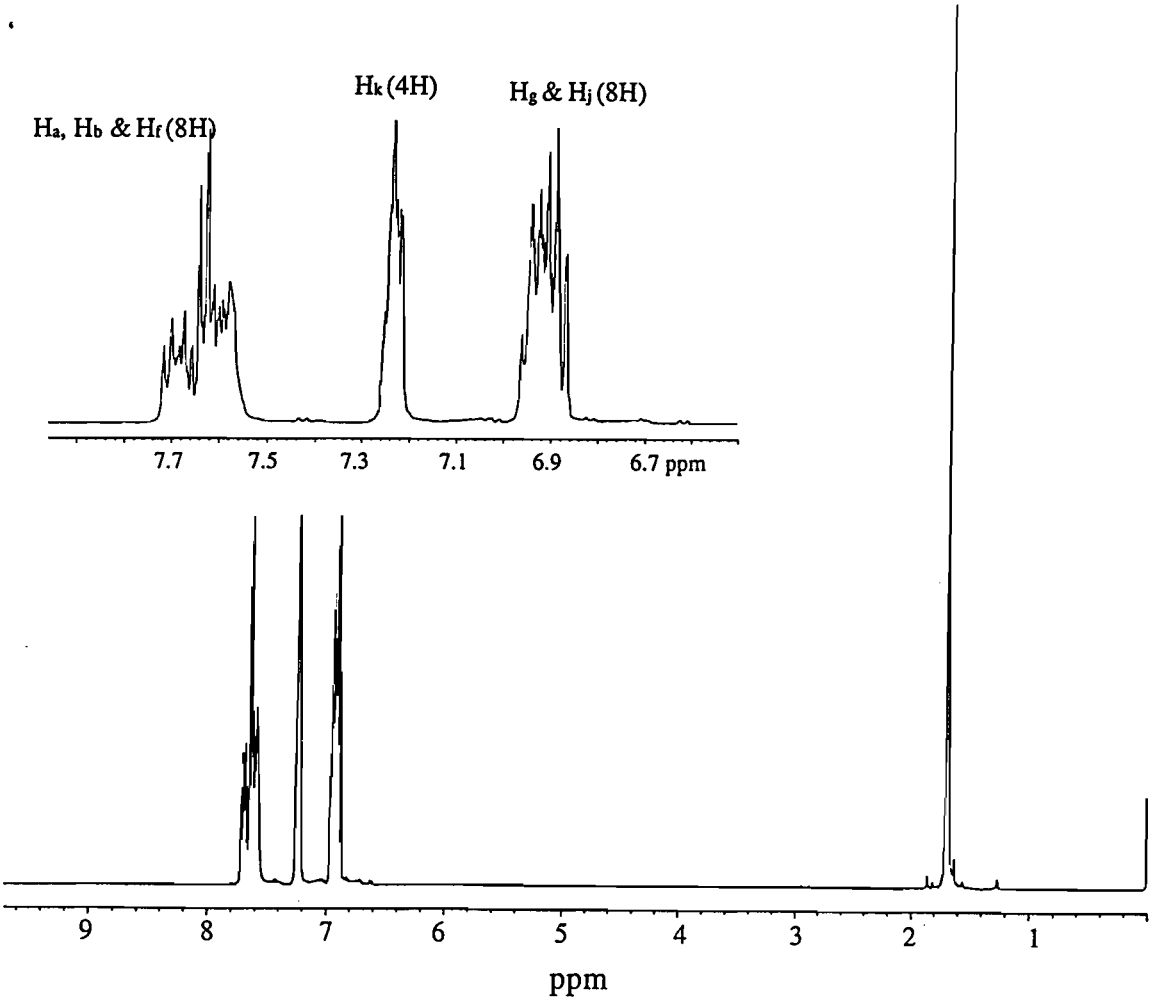
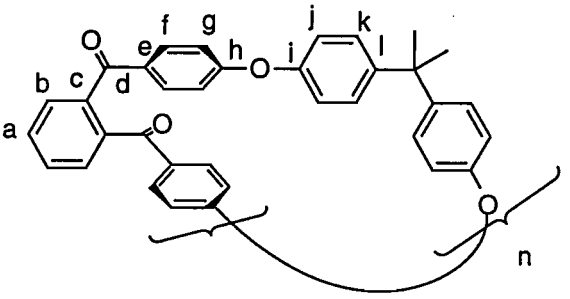


^{13}C NMR (125 MHz, $CDCl_3$) of cyclic oligomer 2.8c.



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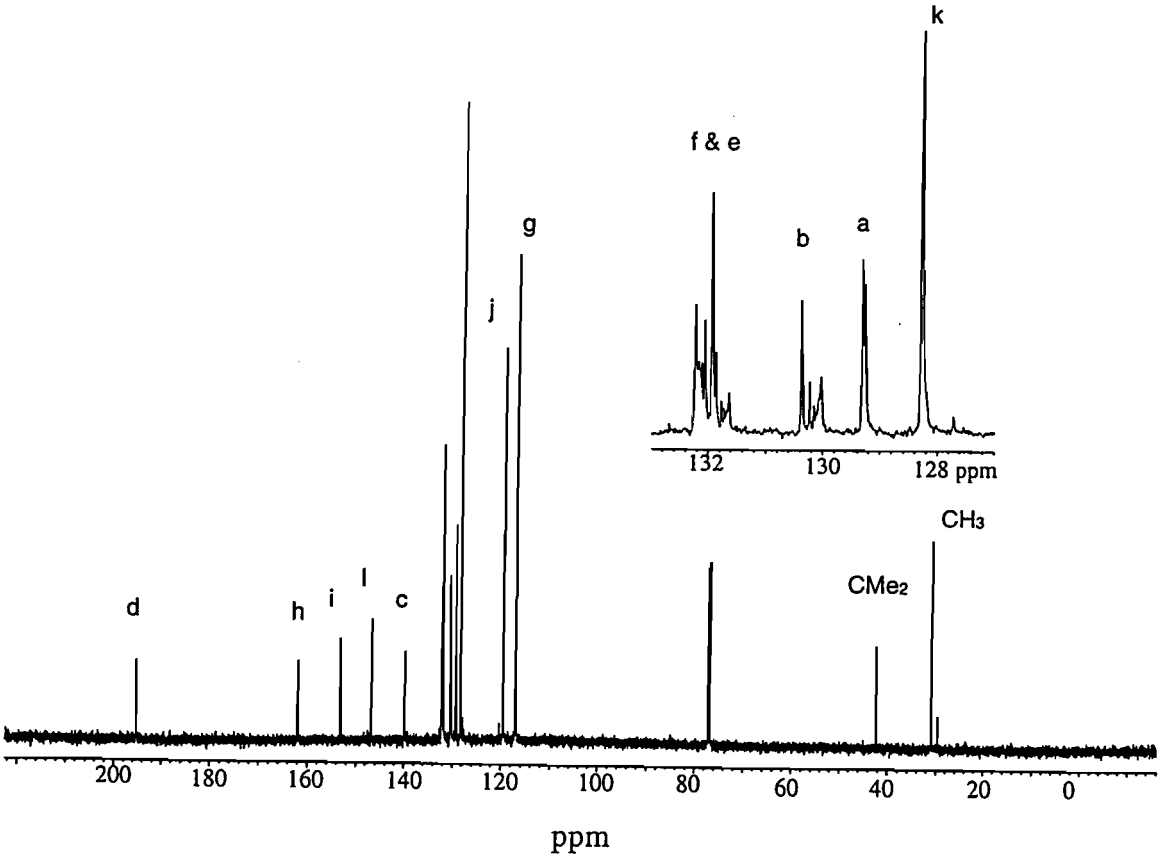
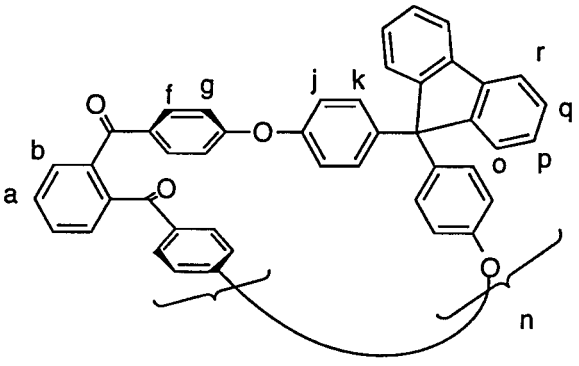
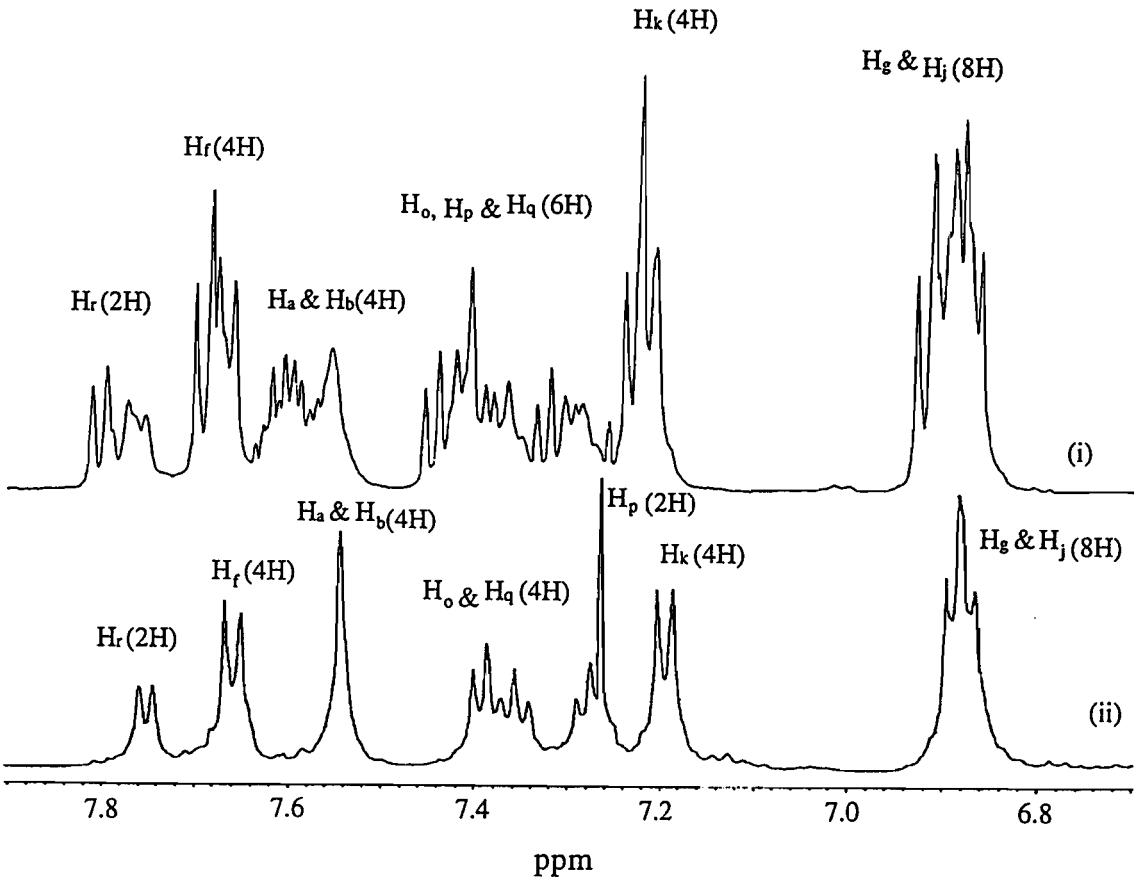


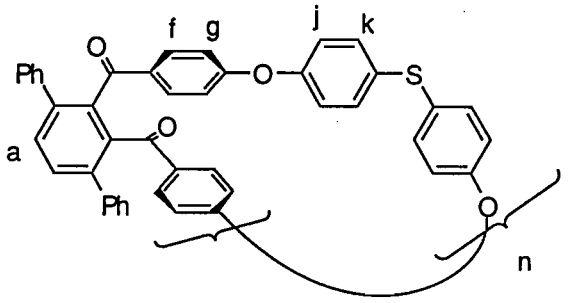
^{1}H NMR (500 MHz, $CDCl_3$) of (i) cyclic oligomer 2.8d and (ii) its corresponding linear polymer.



2.8d



^{1}H NMR (500 MHz, $CDCl_3$) of cyclic oligomer 2.9b.



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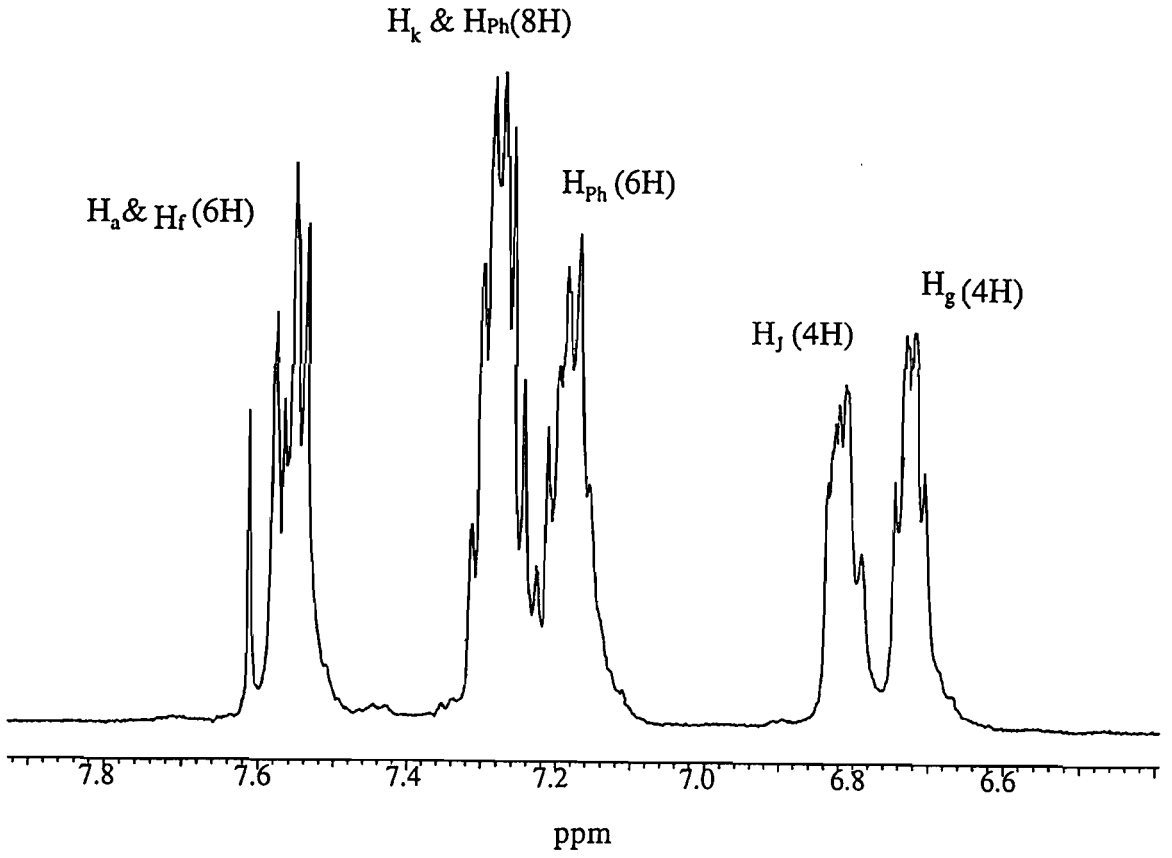

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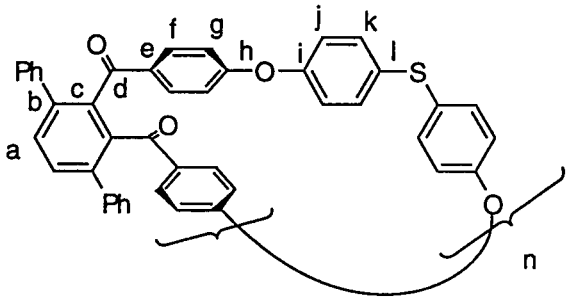

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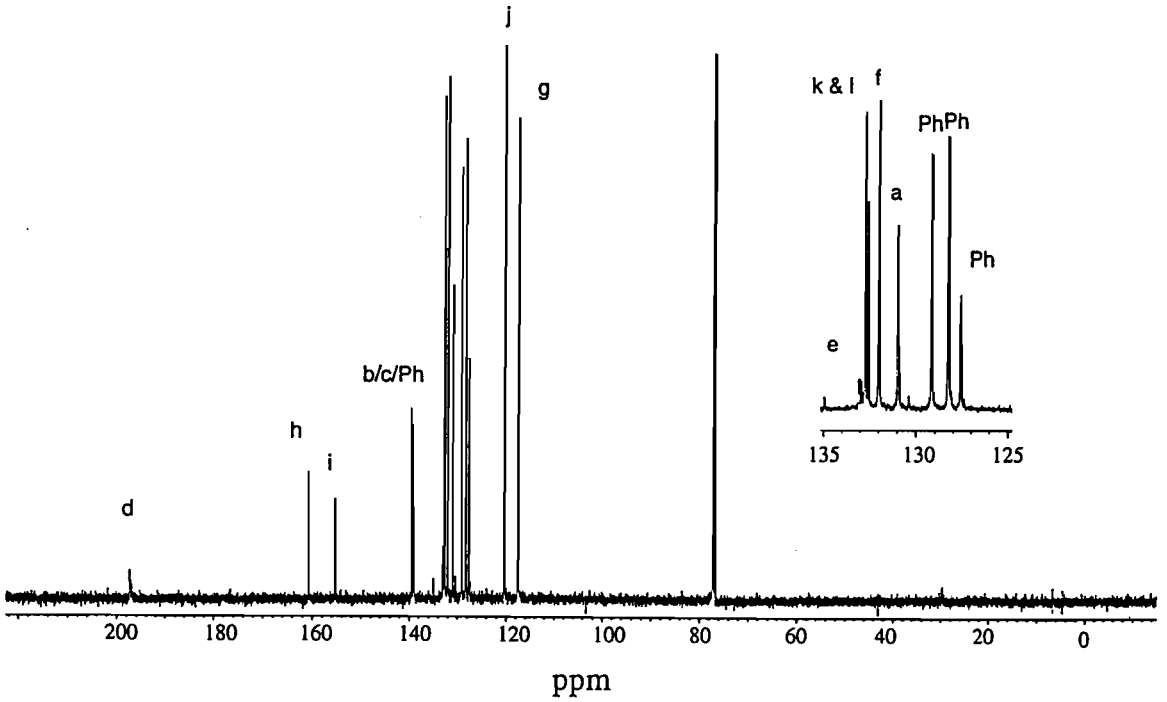

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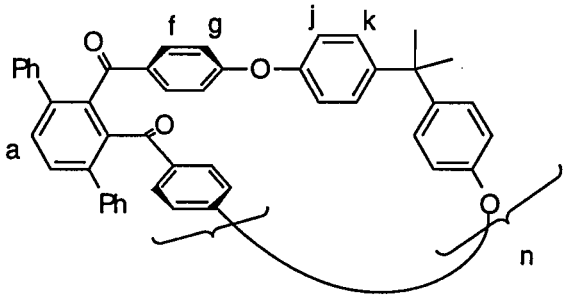

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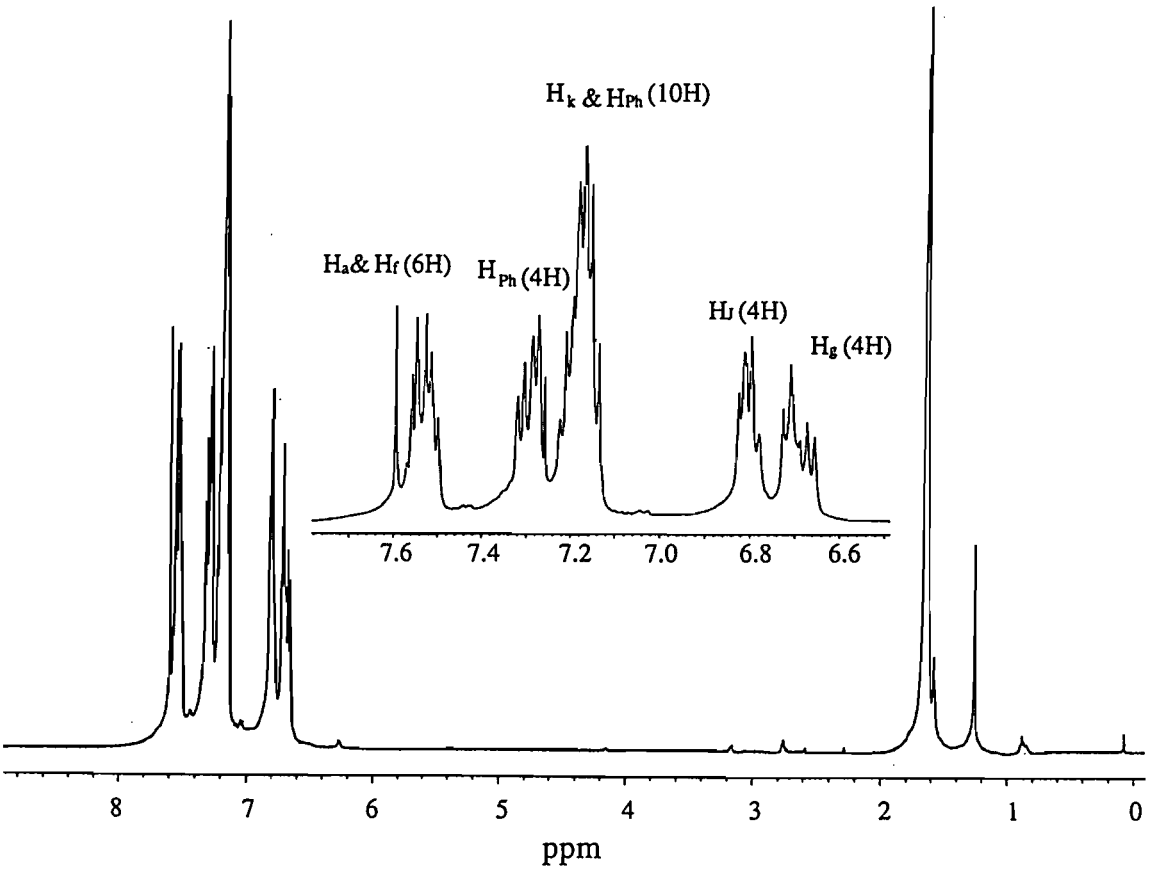

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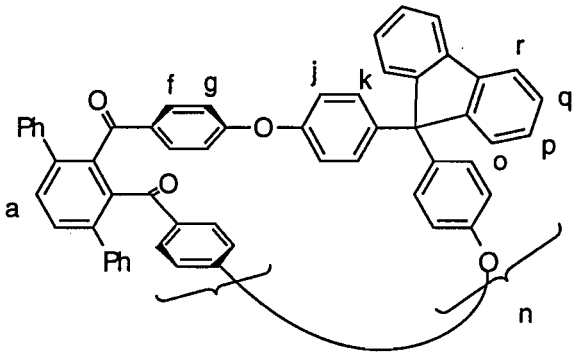

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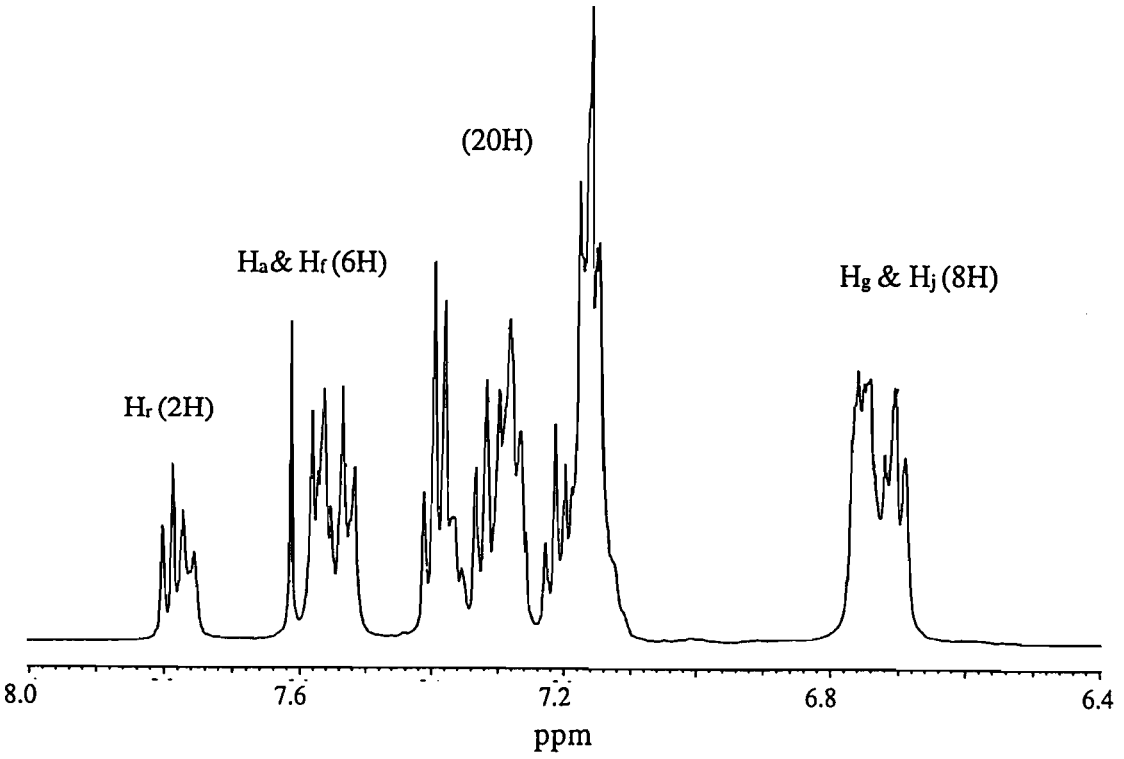
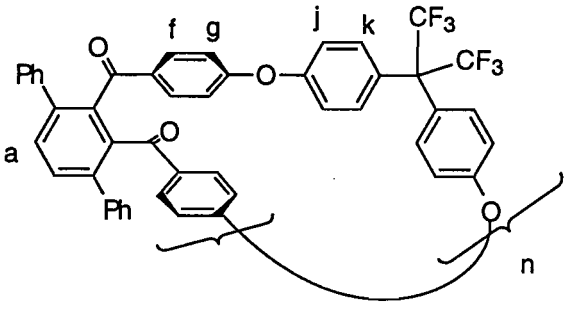


^{1}H NMR (500 MHz, $CDCl_3$) of cyclic oligomer 2.9e.



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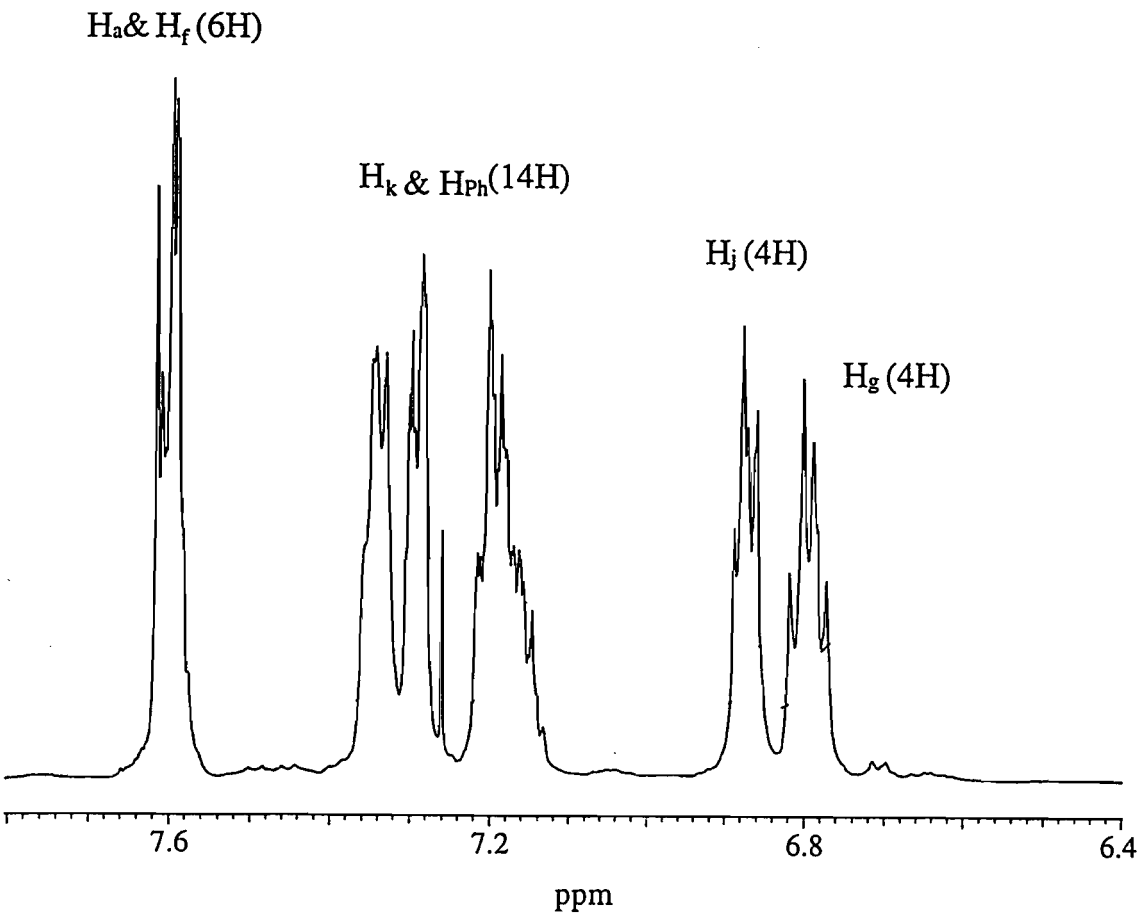

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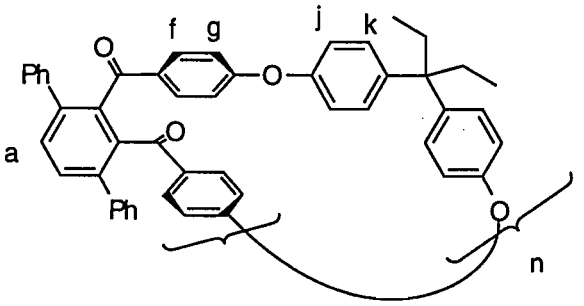

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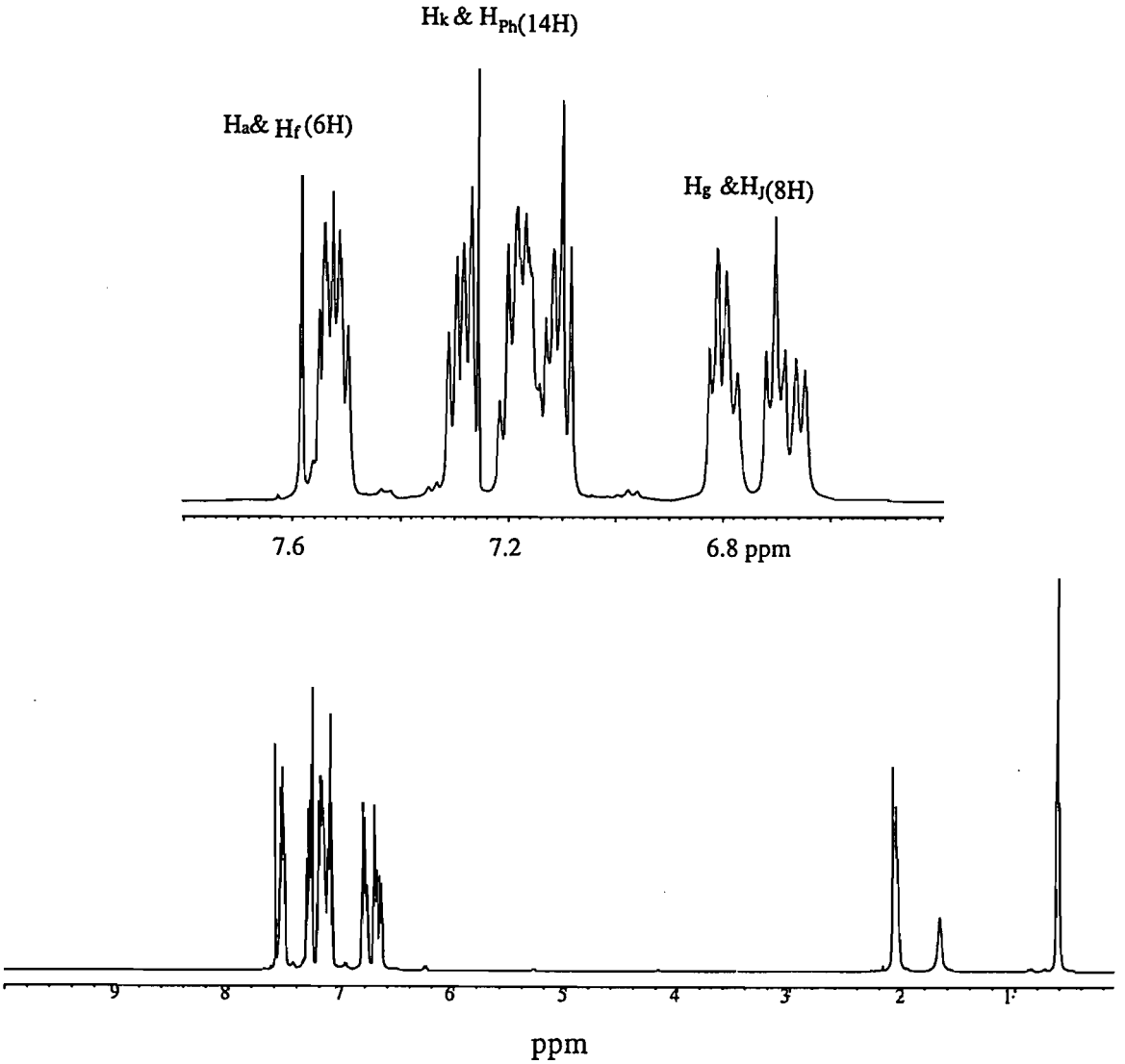

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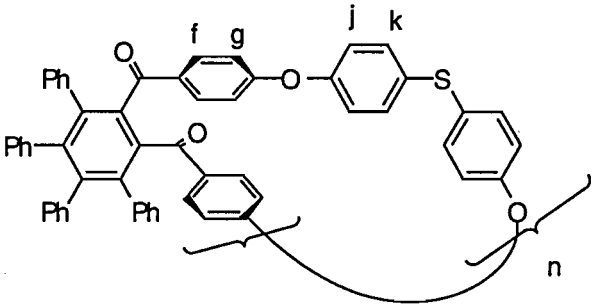
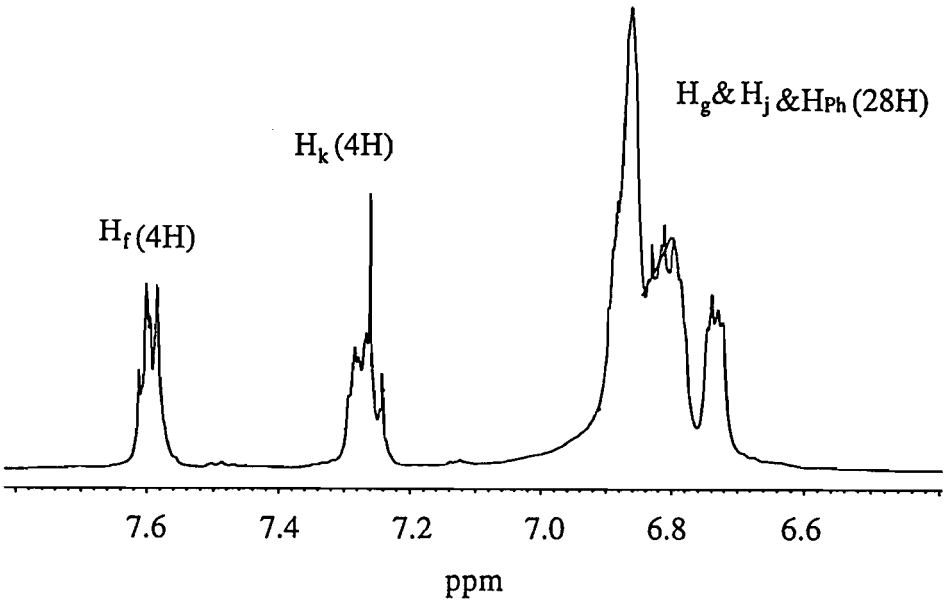
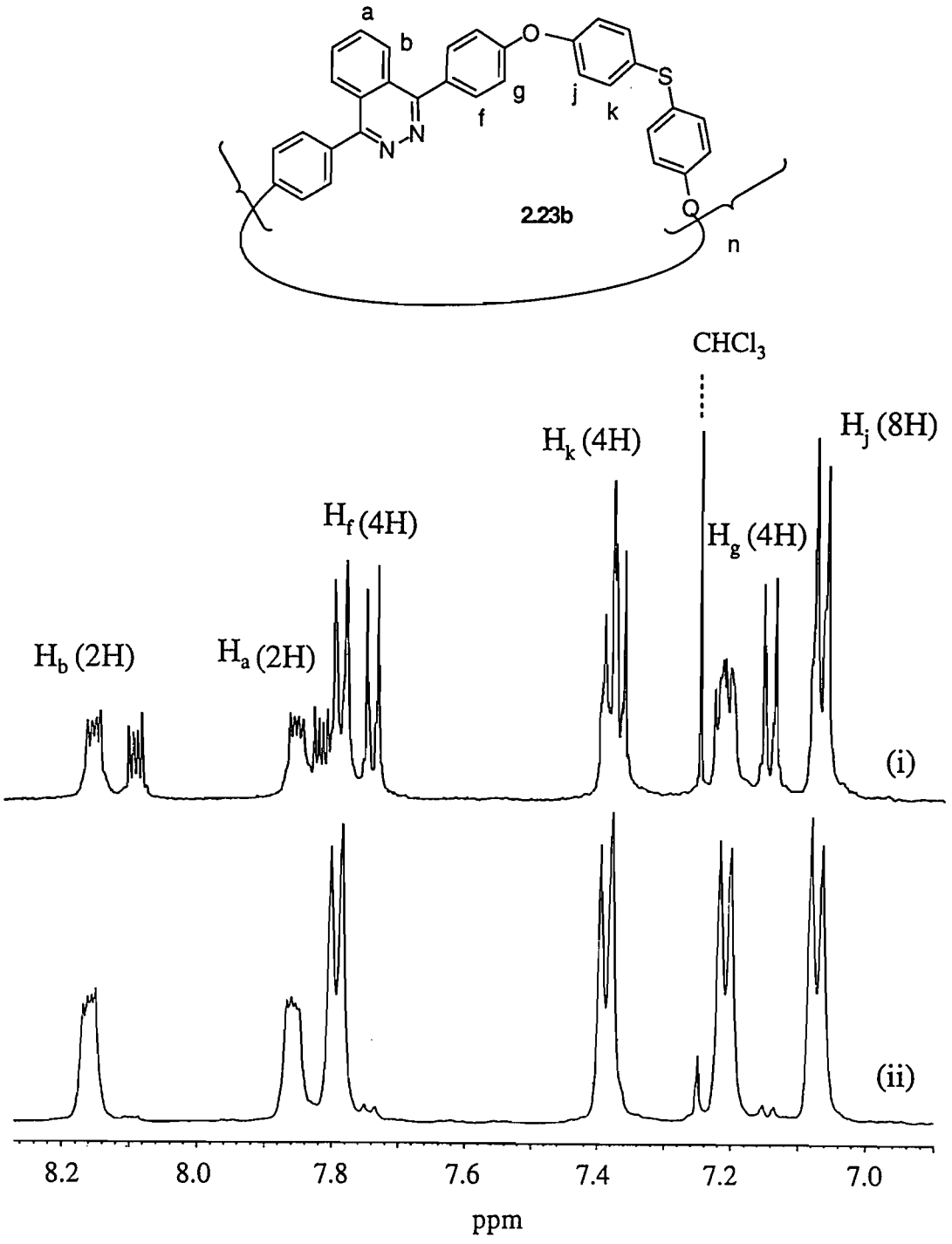


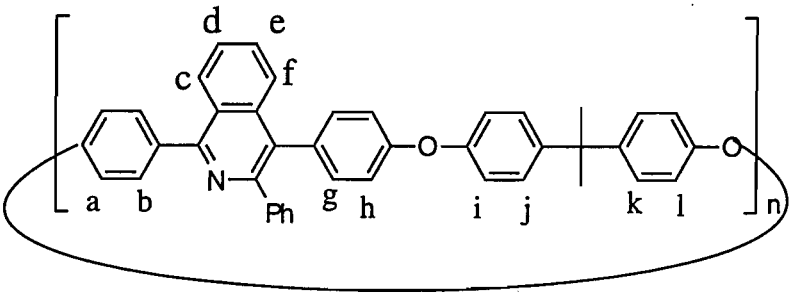
2.10b



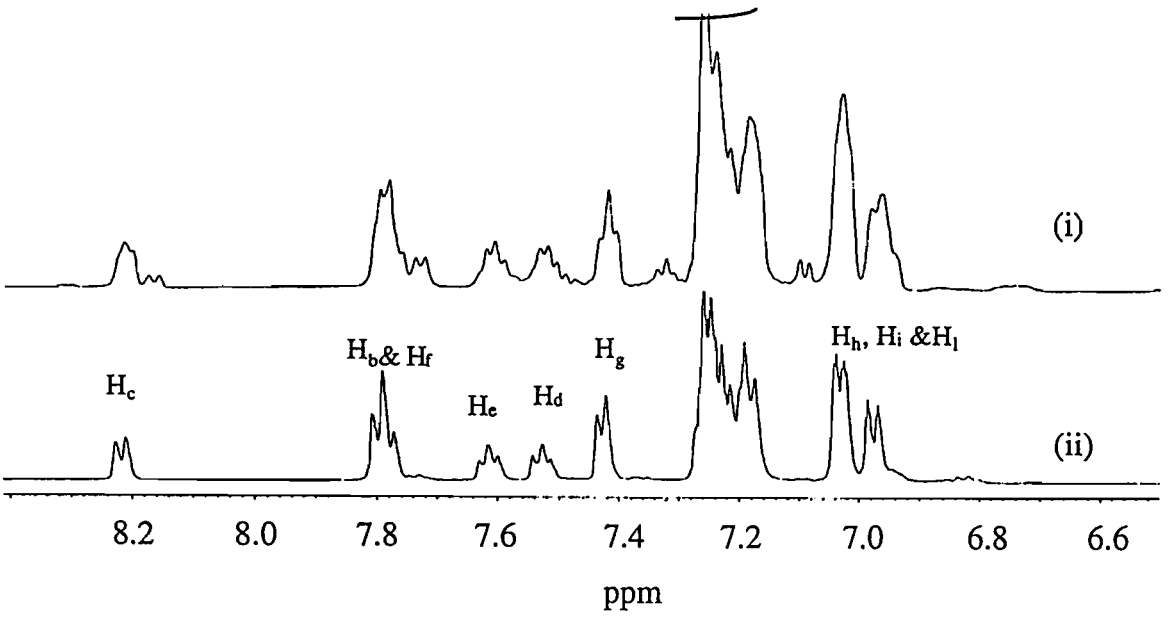
^{1}H NMR (500 MHz, $CDCl_3$) of (i) cyclic oligomer 2.23b, and (ii) it corresponding linear polymer.



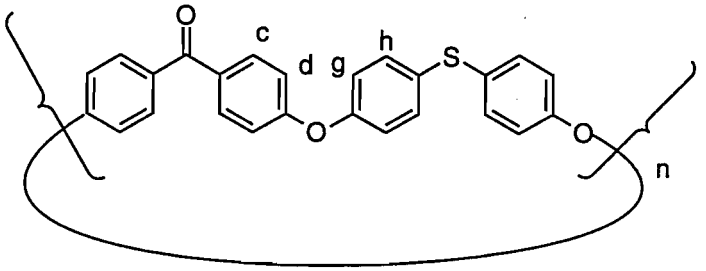
^{1}H NMR (500 MHz, $CDCl_3$) of (i) cyclic oligomer 2.24c, and (ii) its corresponding linear polymer.



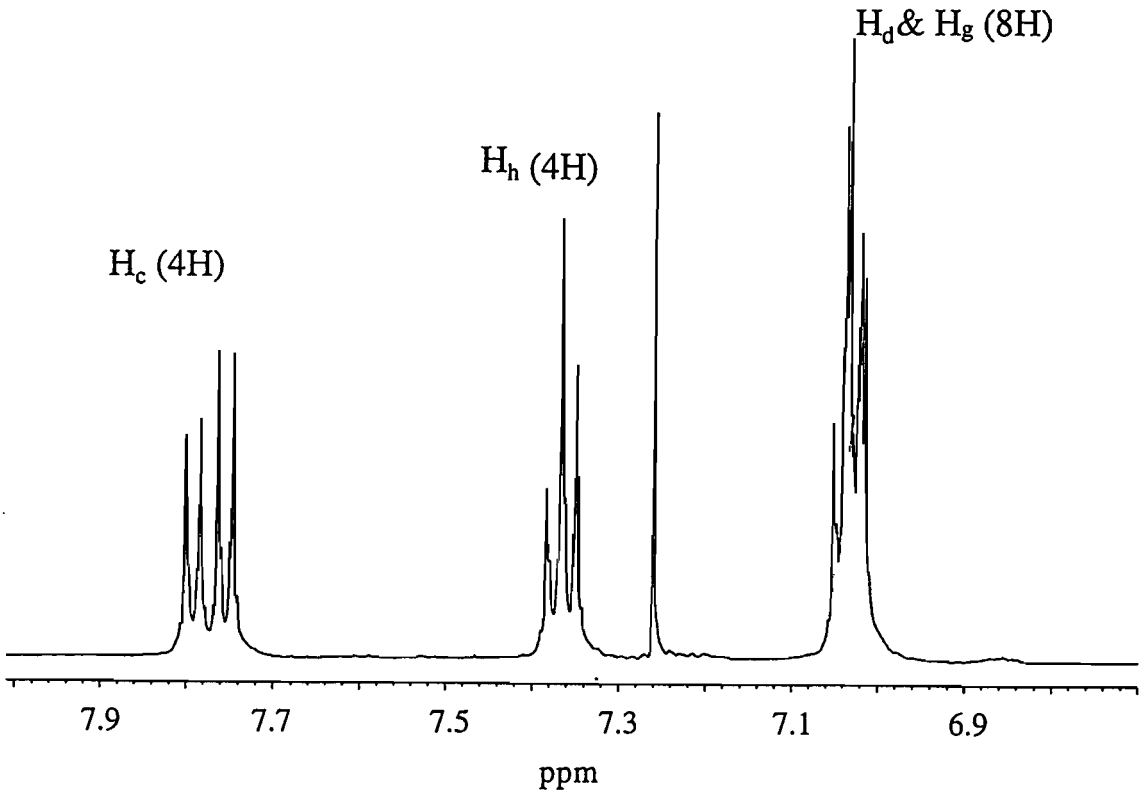
2.24c



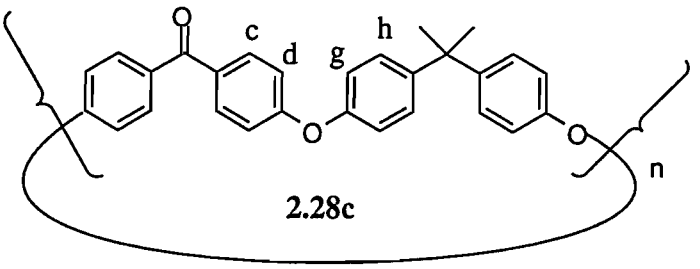
^{1}H NMR (500 MHz, $CDCl_3$) of cyclic oligomer 2.28b.



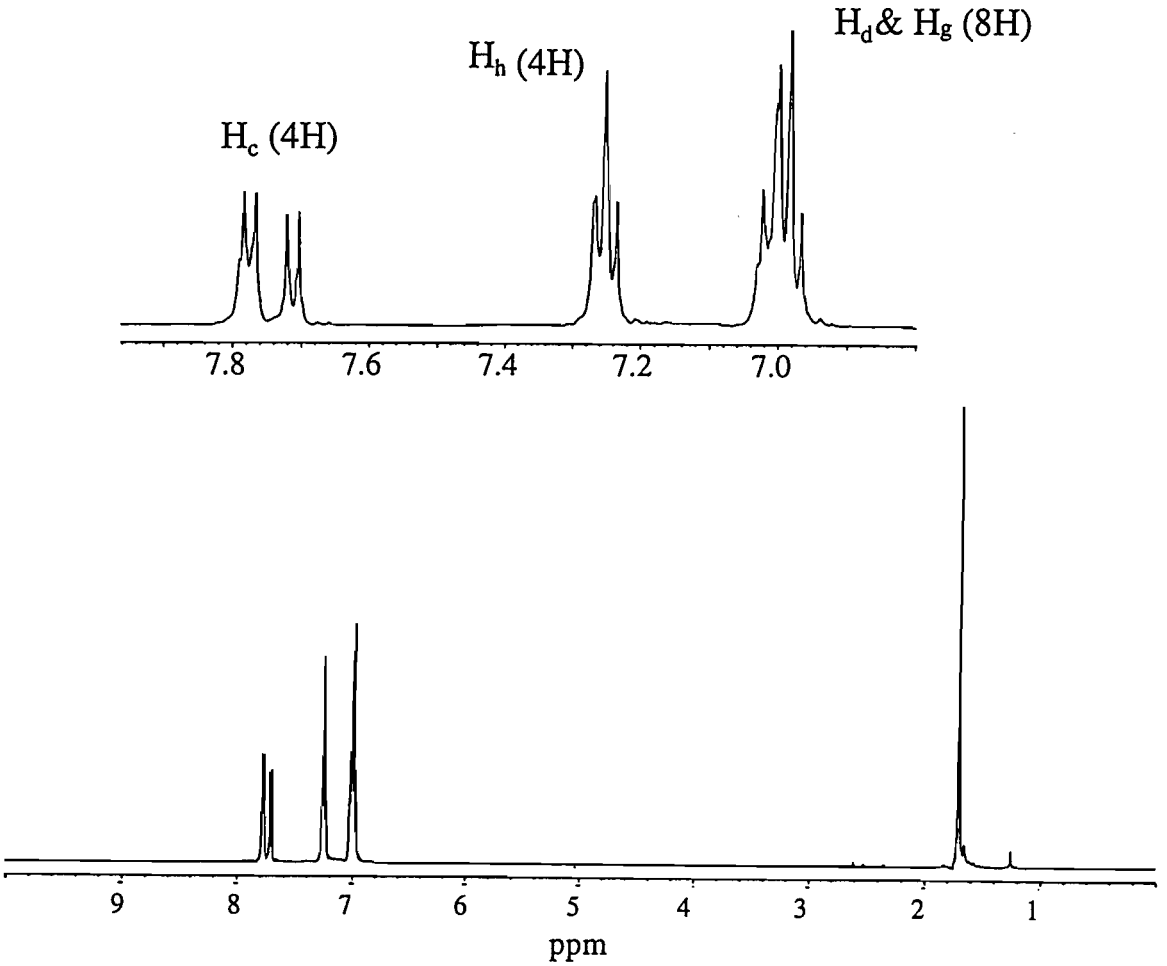
2.28b



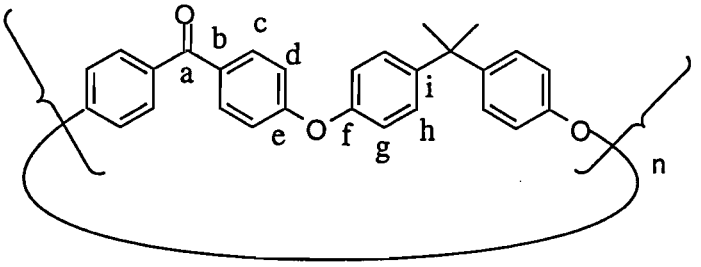
^{1}H NMR (500 MHz, $CDCl_3$) of cyclic oligomer 2.28c.



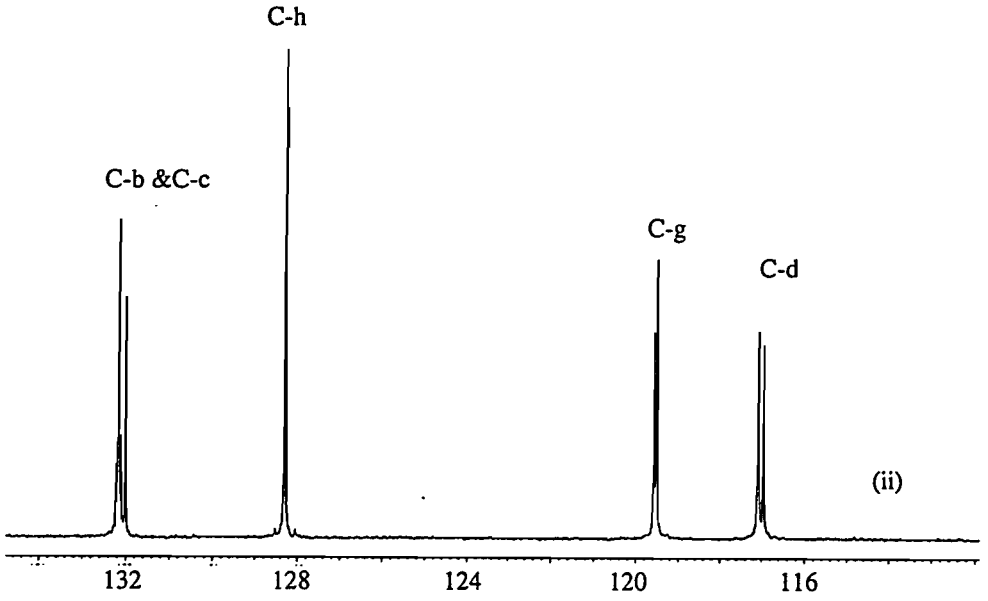
2.28c

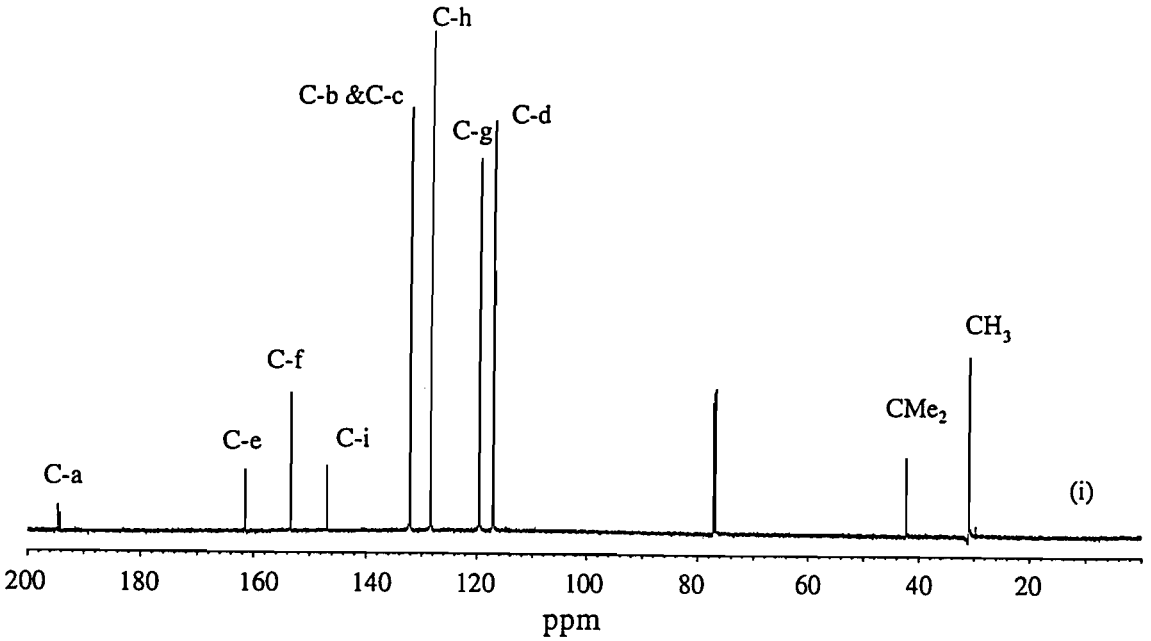


^{13}C NMR (125 MHz, $CDCl_3$) of (i) cyclic oligomer 2.28c, and (ii) expansion.

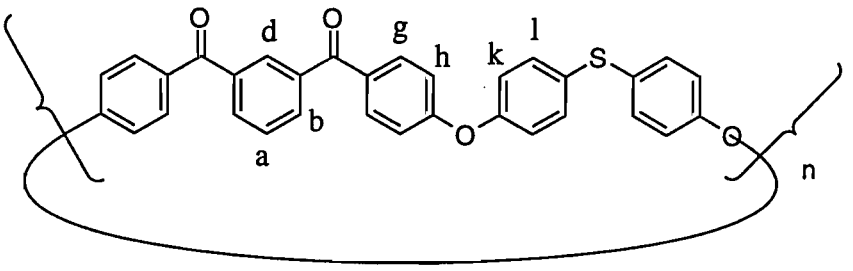


2.28c

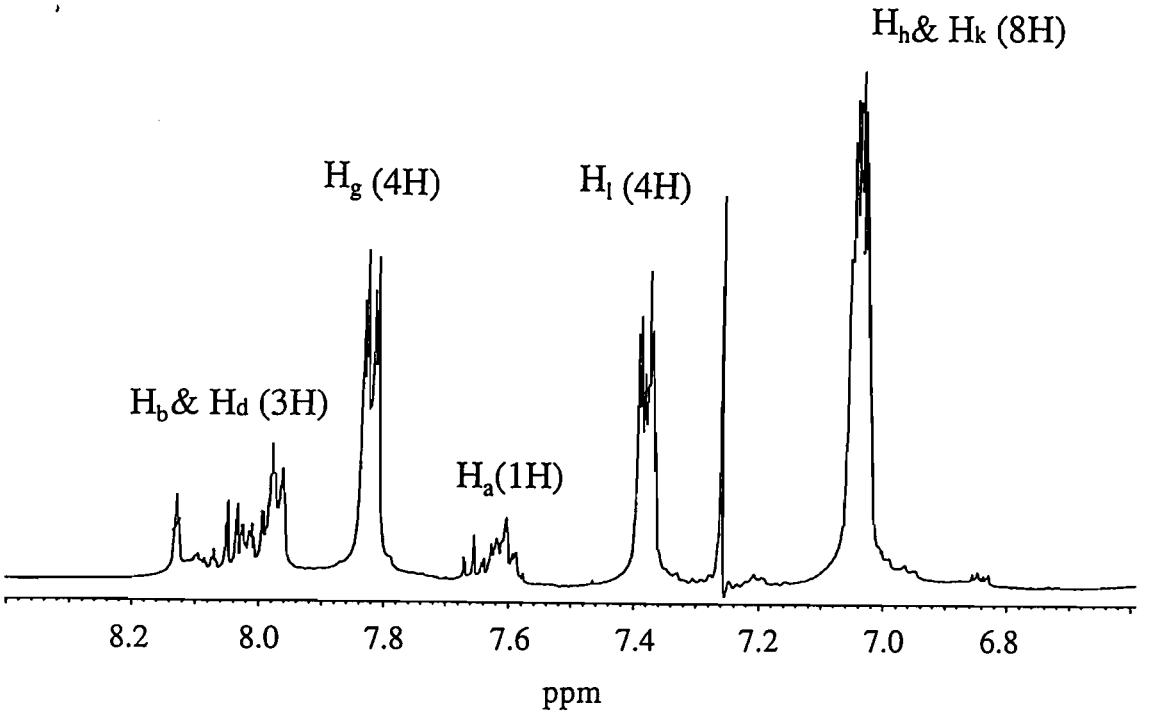




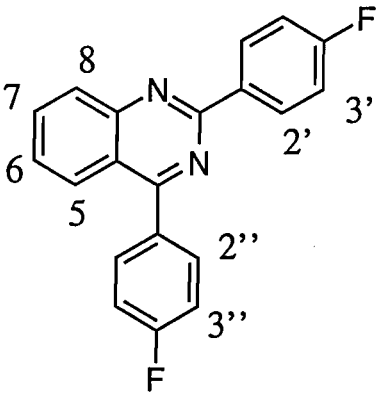
^{1}H NMR (500 MHz, $CDCl_3$) of cyclic oligomer 2.30b.



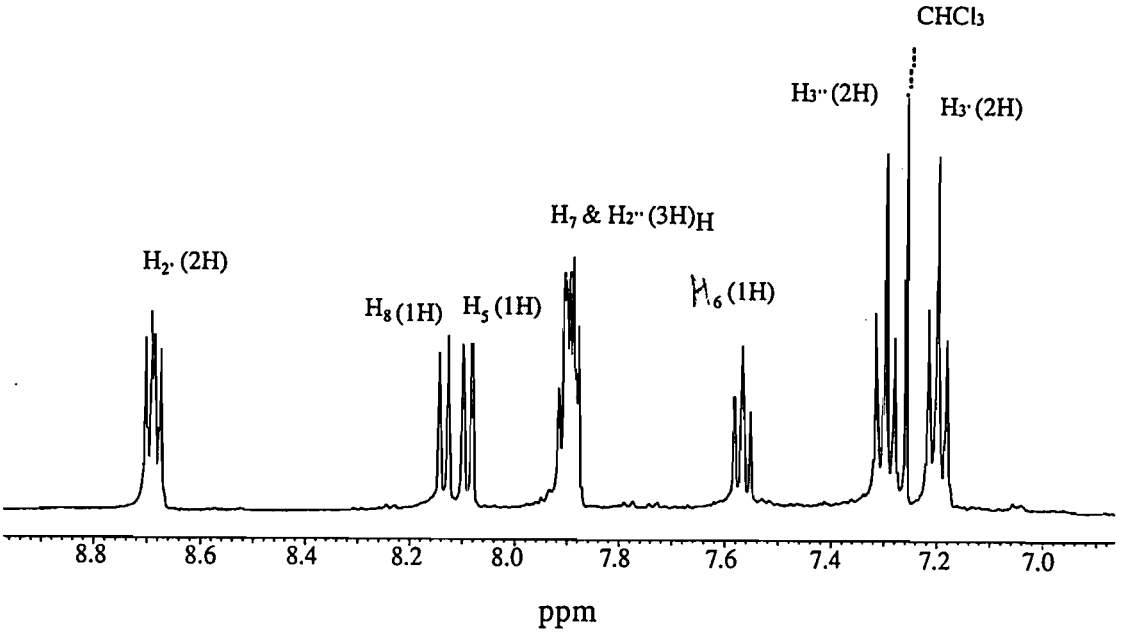
2.30b



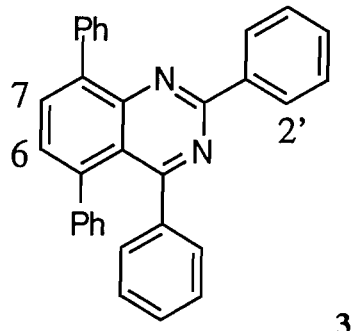
^{1}H NMR (500 MHz, $CDCl_3$) of 3.9a.



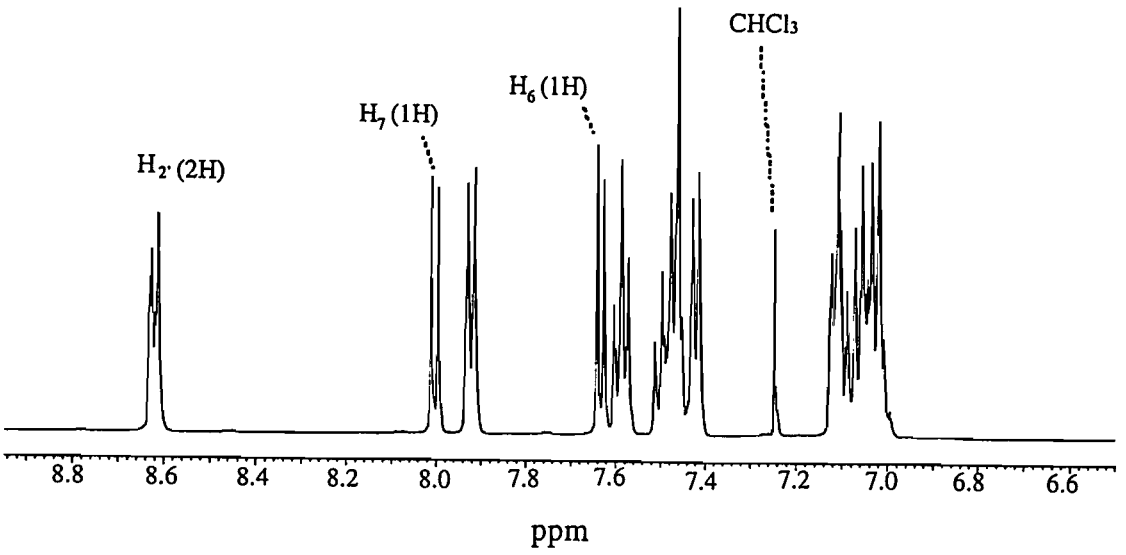
3.9a



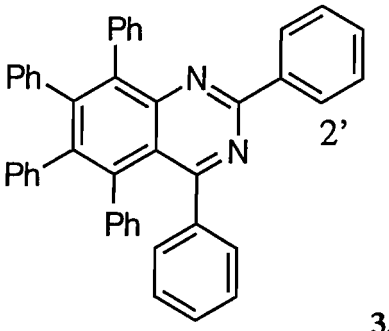
^{1}H NMR (500 MHz, $CDCl_3$) of 3.9b.



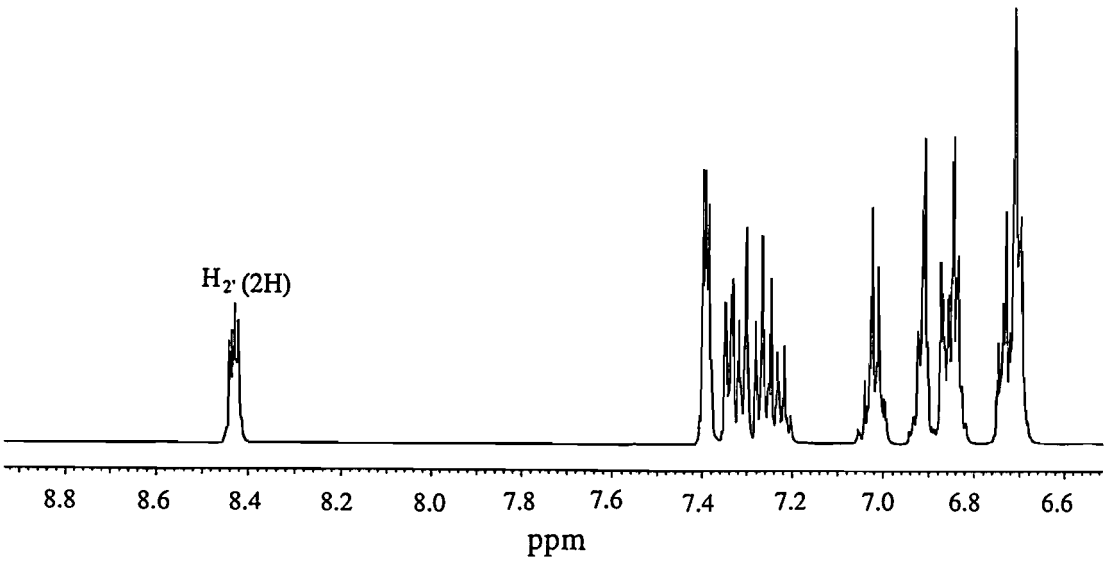
3.9b



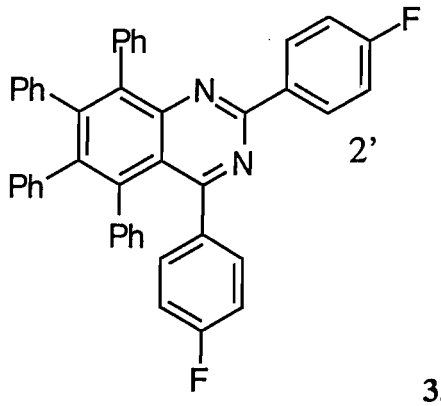
^{1}H NMR (500 MHz, $CDCl_3$) of 3.9c.



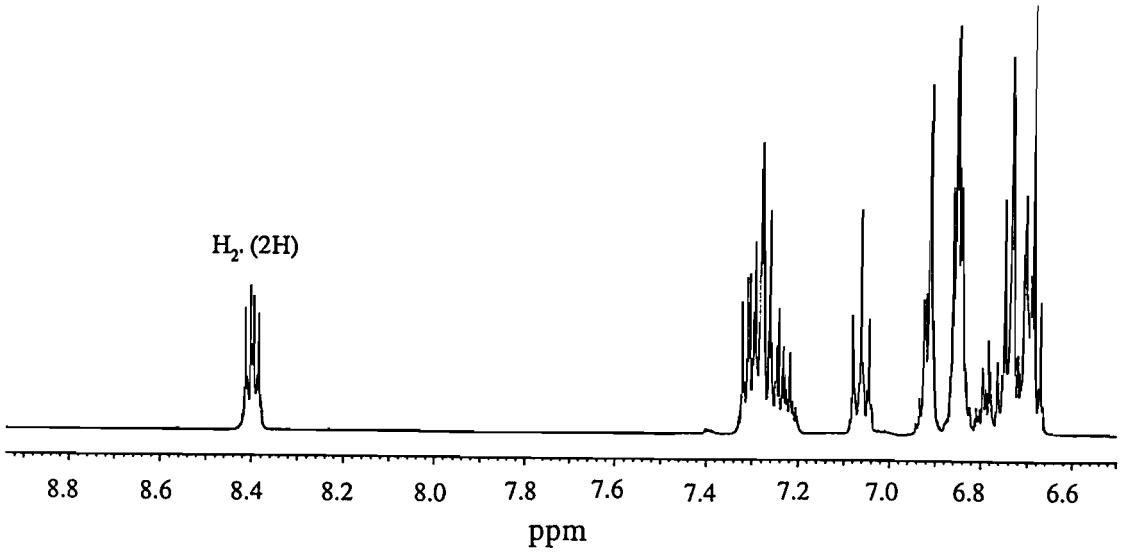
3.9c

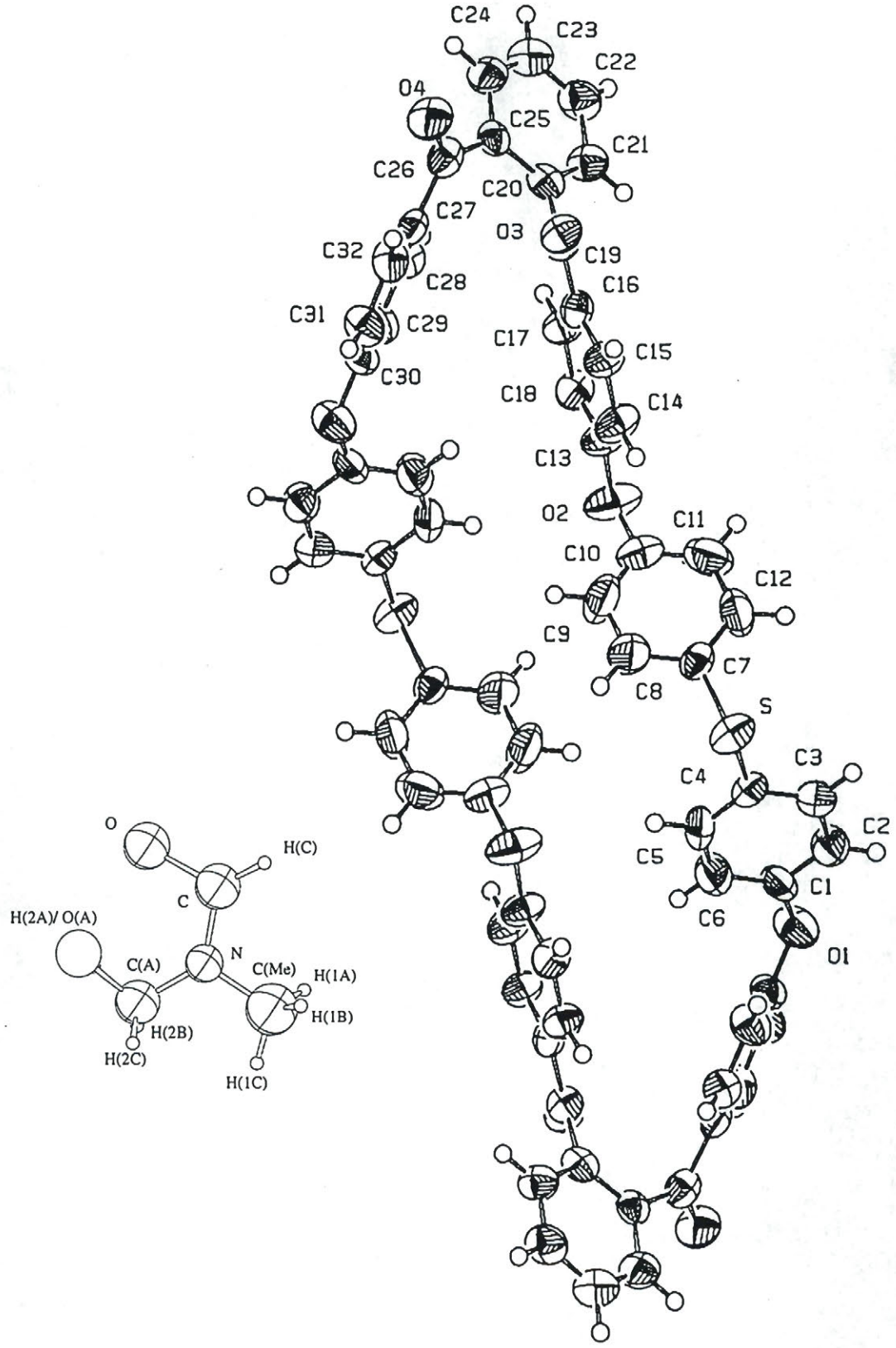


^{1}H NMR (500 MHz, $CDCl_3$) of 3.9d.



3.9d

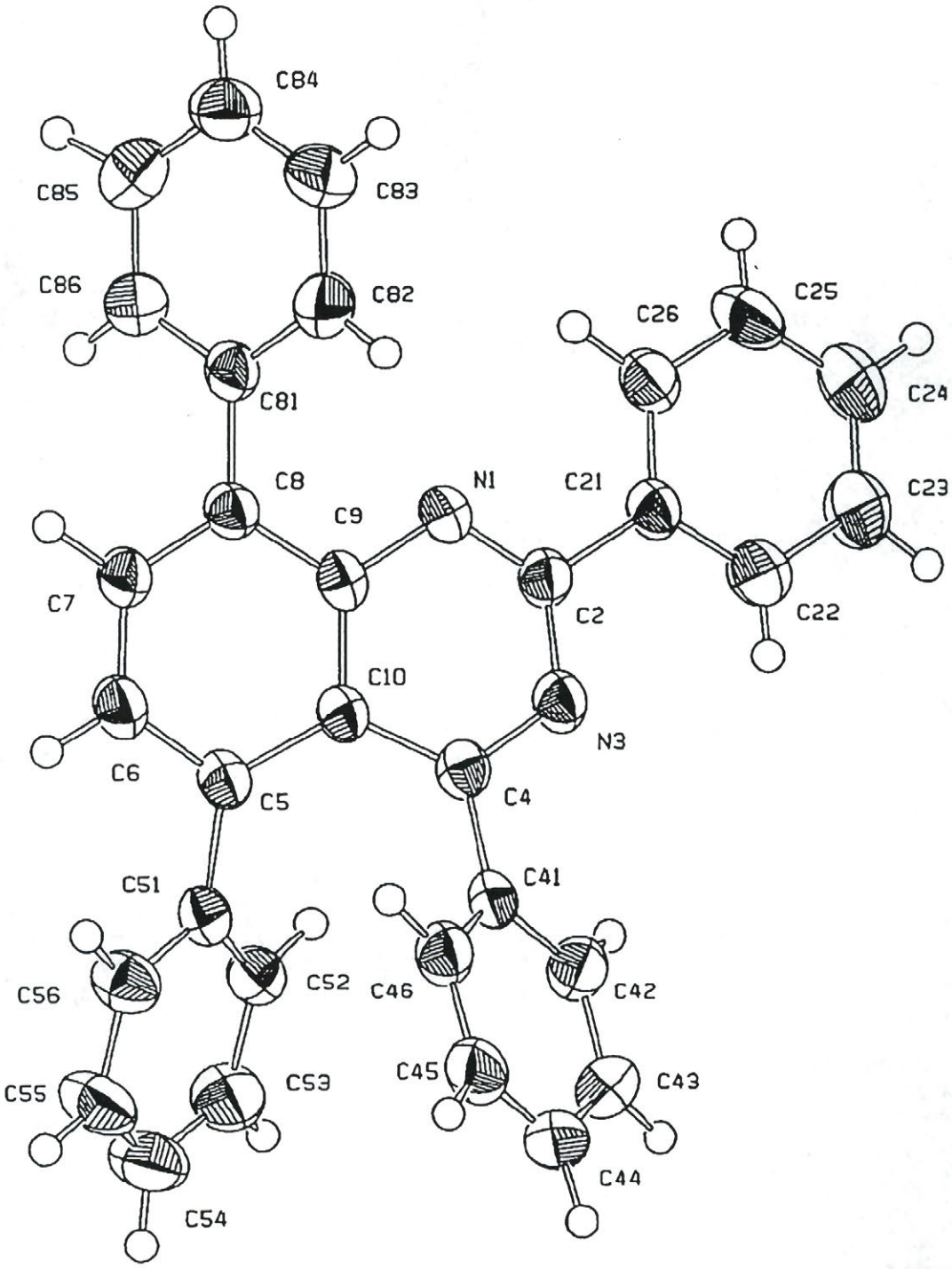



C24
C23
C22
O4
C25
C21
C26
C20
C27
O3
C32
C19
C28
C16
C31
C29
C17
C15
C30
C18
C14
C13
O2
C11
C10
C12
C9
C7
C8
S
C3
C4
C2
C5
C1
C6
O1
O
H(C)
C
H(2A)/ O(A)
N
C(A)
C(Me)
H(1A)
H(1B)
H(2B)
H(2C)
H(1C)

Positional Parameters for Cyclic Dimer of **2.8b** $C_{64}H_{40}O_8S_2$.DMF.

atom	z	y	z	occupancy
S	0.42523(09)	0.21832(17)	0.35209(17)	
0(1)	0.3330(02)	0.2701(04)	0.7362(04)	
0(2)	0.6296(03)	0.0695(05)	0.4898(05)	
0(3)	0.7889(02)	0.0318(04)	0.1630(04)	
0(4)	0.8726(02)	-0.1282(04)	0.0981(04)	
C(1)	0.3534(03)	0.2553(06)	0.6455(07)	
C(2)	0.3733(04)	0.3222(06)	0.5995(07)	
C(3)	0.3967(03)	0.3113(06)	0.5117(07)	
C (4)	0.3996(03)	0.2318(06)	0.4693(06)	
C(S)	0.3792(04)	0.1653(06)	0.5171(08)	
C(6)	0.3567(04)	0.1763(07)	0.6074(08)	
C (7)	0.4879(04)	0.1746(06)	0.3907(06)	
C(8)	0.4953(04)	0.0895(07)	0.3864(09)	
C(9)	0.5432(05)	0.0556(07)	0.4180(09)	
C (10)	0.5826(04)	0.1041(08)	0.4500(08)	
C(11)	0.5770(04)	0.1896(08)	0.4513(09)	
C(12)	0.5283(04)	0.2246(06)	0.4193(08)	
C (13)	0.6690(03)	0.0632(06)	0.4275(07)	
C(14)	0.6654(03)	0.0863(06)	0.3295(07)	
C (15)	0.7074(03)	0.0751(06)	0.2748(06)	
C(16)	0.7537(03)	0.0406(05)	0.3188(06)	
C(17)	0.7557(03)	0.0170(06)	0.4176(07)	
C(18)	0.7144(04)	0.0270(06)	0.4733(06)	
C(19)	0.7961(03)	0.0265(06)	0.2534(06)	
C(20)	0.8506(03)	0.0072(06)	0.2992(06)	
C(21)	0.8748(04)	0.0572(06)	0.3728(07)	
C(22)	0.9273(04)	0.0475(07)	0.4038(07)	
C(23)	0.9549(04)	-0.0110(07)	0.3550(08)	
C(24)	0.9317(04)	-0.0626(06)	0.2820(07)	
C(25)	0.8788(04)	-0.0552(05)	0.2523(06)	
C(26)	0.8545(04)	-0.1143(06)	0.1783(07)	
C(27)	0.8055(03)	-0.1600(05)	0.2012(06)	
C(28)	0.7960(03)	-0.1739(06)	0.2991(06)	
C(29)	0.7510(04)	-0.2130(06)	0.3238(07)	
C(30)	0.7139(04)	-0.2324(06)	0.2484(07)	
C(31)	0.7229(04)	-0.2218(06)	0.1490(07)	
C(32)	0.7689(04)	-0.1853(06)	0.1262(07)	
0	0.4601(10)	0.0854(19)	0.769(02)	1/2
N	1/2	0.2025(16)	3/4	1/2
C	0.4682(09)	0.1686(15)	0.8074(18)	
C((Me))	1/2	0.289(03)	3/4	1/2

The DMF molecule is disordered, N and C(Me) are on the two-fold axis, positions C and C(A) are alternately the carbonyl and methyl carbons, O(A) atom is the position in the mirror image.


C84
C85
C83
C86
C82
C81
C8
C9
N1
C21
C26
C25
C24
C23
C22
C7
C2
C10
N3
C6
C5
C4
C51
C41
C56
C52
C46
C42
C55
C53
C45
C43
C54
C44

Positional parameters for **3.9b**, C32H22N2

atom	x	y	z
N(1)	0.0066(02)	-0.0475(02)	0.1319(02)
N(3)	0.0662(02)	-0.1604(02)	0.0440(02)
C(2)	0.0636(02)	-0.0920(02)	0.0932 (03)
C(4)	0.0088(02)	-0.1818(02)	0.0238(02)
C(5)	-0.1124(02)	-0.1376 (02)	0.0138(02)
C(6)	-0.1712(02)	-0.0896(02)	0.0568(03)
C(7)	-0.1743(02)	-0.0343(02)	0.1277(03)
C(8)	-0.1166(02)	-0.0201(02)	0.1558(02)
C(9)	-0.0534(02)	-0.0669(02)	0.1110(03)
C(10)	-0.0523(02)	-0.1295(02)	0.0462(02)
C(21)	0.1312(02)	-0.0668(02)	0.1061(03)
C(22)	0.1943(02)	-0.1070(03)	0.0604(04)
C(23)	0.2582(03)	-0.0794(04)	0.0675(05)
C(24)	0.2588(03)	-0.0136(03)	0.1209(04)
C(25)	0.1962(03)	0.0271(03)	0.1672(04)
C(26)	0.1323(02)	-0.0003(03)	0.1604(03)
C(41)	0.0134(02)	-0.2630(02)	-0.0176(02)
C(42)	0.0769(02)	-0.2888(03)	-0.0854(03)
C(43)	0.0826(03)	-0.3641(03)	-0.1242(03)
C(44)	0.0265(03)	-0.4162(03)	-0.0959(04)
C(45)	-0.0366(03)	-0.3931(03)	-0.0246(04)
C(46)	-0.0433(02)	-0.3169(02)	0.0130(03)
C(51)	-0.1132(02)	-0.1875(02)	-0.0680(03)
C(52)	-0.0557(02)	-0.1884(02)	-0.1529(03)
C(53)	-0.0605(03)	-0.2303(03)	-0.2299(03)
C(54)	-0.1221(03)	-0.2718(03)	-0.2230(04)
C(55)	-0.1785(03)	-0.2715(03)	-0.1404(03)
C(56)	-0.1747(02)	-0.2301(03)	-0.0619(03)
C(81)	-0.1205(02)	0.0415(02)	0.2292(03)
C(82)	-0.0972(02)	0.0263(03)	0.3050(03)
C(83)	-0.1024(03)	0.0841(03)	0.3728(03)
C(84)	-0.1318(02)	0.1573(03)	0.3681(03)
C(85)	-0.1559(02)	0.1732(03)	0.2946(03)
C(86)	-0.1511(02)	0.1150(03)	0.2261(03)
H(6)	-0.212(02)	-0.099(02)	0.039(03)
H(7)	-0.216(02)	0.002(02)	0.155(02)
H(22)	0.197(02)	-0.151(02)	0.025(03)
H(23)	0.297(03)	-0.115(03)	0.036(03)
H(24)	0.303(03)	0.008(03)	0.121(04)
H(25)	0.198(02)	0.076(02)	0.195(03)
H(26)	0.087(02)	0.034(02)	0.197(03)
H(42)	0.115(02)	-0.253(02)	-0.109(03)
H(43)	0.126(02)	-0.378(02)	-0.177(02)
H(44)	0.031(02)	-0.472(02)	-0.118(03)

H(45)	-0.073(02)	-0.435(02)	-0.005(03)
H(46)	-0.088(02)	-0.299(02)	0.068(02)
H(52)	-0.013(02)	-0.154(02)	-0.157(03)
H(53)	-0.023(02)	-0.231(02)	-0.285(03)
H(54)	-0.122(02)	-0.307(03)	-0.271(03)
H(55)	-0.222(02)	-0.304(02)	-0.134(03)
H(56)	-0.217(02)	-0.227(02)	-0.001(03)
H(82)	-0.080(02)	-0.025(02)	0.308(02)
H(83)	-0.089(03)	0.071(03)	0.425(04)
H(84)	-0.135(02)	0.199(02)	0.410(03)
H(85)	-0.180(02)	0.226(02)	0.284(03)
H(86)	-0.163(02)	0.127(03)	0.171(03)