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New Polymerization Reactions.

Sulfur Containing Cyclic Oligomers and High Performance Polymers

By

Yong Ding

A thesis submitted to the Faculty of Graduate Studies and Research in partial fulfillment of the requirements for the degree of Doctor of Philosophy

Department of Chemistry
McGill University
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To:

my parents, wife and daughter shensi

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Last, but not least, I am grateful to my wife for her years of full support, endeavor and sharing of success or failure.

Abstract

Sulfur containing polymers are very important as rubbers, conducting materials, and high performance polymers. Examples are poly(aliphatic disulfide)s, poly(phenylene sulfide) (PPS), poly(sulfone), and polybenzothiazole. Several new polymerization reactions have been described in this thesis for the preparation of sulfur containing materials.

The synthesis of a series of cyclic(arylene disulfide) oligomers was accomplished by catalytic oxidation of arylenedithiols with oxygen in the presence of a copper-amine catalyst. The cyclic(arylene disulfide) oligomers underwent a novel free radical ring-opening polymerization at elevated temperatures in the melt to form high molecular weight poly(arylene disulfide)s. Cyclic(arylene disulfide) oligomers were copolymerized with elemental sulfur at 250 ℃ to form stable poly(arylene sulfane)s containing 3-7 sulfur linkages. They also copolymerized with diiodoaromatic compounds, or dibromoaromatic compounds, in the presence of potassium iodide at 270 ℃ to give poly(thioarylene)s with the formation of iodine as the coproduct in both cases.

The novel self-polymerization of 4-bromobenzenethiol was realized at 270 ℃ in *m*-terphenyl solution in the presence of a catalytic amount of free radical initiator. Hydrogen bromide is the sole side product. This novel reaction has also been extended to the synthesis of poly(thioarylene)s from arylenedithiols and dibromoaromatic compounds.

Another novel polymerization reaction to prepare poly(arylene thioether)s has been realized by a one-pot reaction of bis(N,N'-dimethyl-S-carbamate)s with activated dihalocompounds in diphenylsulfone in the presence of a mixture of Cs_2CO_3/$CaCO_3$. Bis(N,N'-dimethyl-S-carbamate)s can be conveniently prepared from dihydroxy compounds *via* the Newman-Kwart rearrangement reaction. This polymerization reaction opens a new route for the synthesis of new poly(arylene thioether)s and poly(arylene sulfone)s.

A series of novel cyclic(arylene ether)s has also been synthesized and characterized. The ring-opening polymerization of these cyclic oligomers in the melt represents a new way to prepare high performance polymers.

Sommaire

Plusieurs réactions de polymérisation ont été descrites dans cette thèse.

La synthèse d'une série d'oligomers (arylène disulfides) cycliques fût accomplie par oxydation catalytique d'arylène dithioles avec l'oxygene en présence d'un catalyseur cuivre-amine.

Les oligomers cycliques (arylène disulfides) subissent une nouvelle polymerisation, par ouveture cyclique de radical libre à hautes températures dans la fonte, pour former des poly(arylene disulfides)s à haut poids moléculaire. Les oligomers cycliques (arylene disulfide) ont été copolymerisés avec le soufre élémentaire à 250°c pour former les poly(arylene sulfane)s contenant des liaisons 3-7 avec le soufre. Ils copolymerisent aussi avec les composés diiodoaromatiques ou les composés dibromoaromatiques en présence de potassium iodine à 270°c pour donner des poly(thioarylene)s avec la formation d'iodine comme coproduit dans les deux cas.

La nouvelle autopolymerisation du 4-bromobenzenethiol a été réalisée à 270°c dans une solution de *m*-terphenyle en présence d'une quantité catalytique d'initiateur en radical libre. Le bromure d'hydrogene est l'unique produit. Cette nouvelle réaction a aussi été étendue pour la synthèse de poly(thioarylene) à partir d'arylenedithiols et de composés dibromoaromatiques.

Une autre réaction de polymérisation été réalisée par "one-pot reaction" pour préparer des ploy(arylene thioether)s à partir de (N,N'-dimethyl-S-carbamate)s avec les dérivés dihalo-activés dans le diphenylsulfone en présence d'un mélange de $Cs_2CO3/CaCO_3$. Le Bis-(N,N'-dimethyl-S-carbamate)s peuvent être conventionnellement preparés à partir de composés dihydroxy via la réaction de réarrangement Newman-Kwart. Cette réaction de polymérisation ouvre une nouvelle route sur la synthèse de nouveaux poly(arylene thioether)s et de poly(arylene sulfone)s.

Un série de nouveaux (arylene ether)s cycliques fûrent synthetisés et carracterisés. La polymérisation par ouverture du cycle pour ces oligomers cycliques dans la fonte représente une nouvelle voie de préparation de polymers à haute performance.

Contributions to Original Knowledge

This thesis describes several new polymerization reactions or processes which are mainly related with sulfur containing polymers. They are briefly summarized as follows.

First, a new class of cyclic oligomers, cyclic(arylene disulfide) oligomers, were synthesized by the oxidation of arylene dithiols with molecular oxygen in the presence of a copper-amine catalyst. The objective was to develop a novel process for preparing poly(arylene disulfide)s. This is the first time that a catalytic system has been used to synthesize cyclic(arylene disulfide)s. The cyclic(arylene disulfide) oligomers were thoroughly characterized with GPC, gradient HPLC, elemental analysis, IR, DSC, TGA, *etc.*.

Cyclic(arylene disulfide) oligomers undergo a novel free-radical ring-opening polymerization reaction to give high molecular weight poly(arylene disulfide)s in the melt as well as in solution. This novel reaction was studied in detail for the cyclic(arylene disulfide) oligomers derived from 4,4'-isopropylidene bis(benzenethiol). The optimum reaction conditions were defined.

Cyclic(arylene disulfide) oligomers react with diiodo aromatic compounds to afford poly(thioarylene)s. They also form high molecular weight poly(thioarylene)s by reacting with dibromo aromatic compounds in the presence of a reducing agent, such as potassium iodide. These novel reactions provide convenient ways to prepare PPS, an important high performance polymer, in the laboratory. Many novel poly(thioarylene)s, which otherwise would be difficult to synthesize, have also been prepared by taking advantage of the new reactions.

We have also found that cyclic(arylene disulfide) oligomers smoothly copolymerize with elemental sulfur in the melt to give high molecular weight, stable poly(arylene sulfane)s. This is the first report on the successful copolymerization of cyclic(disulfide)s with elemental sulfur to give poly(sulfane)s with a large number of sulfur linkages by a free-radical reaction.

The homopolymerization of 4-bromobenzenethiol was realized with a free radical initiator, e.g. bis(4-bromophenyl)disulfide, at 270 °C, with the evolution of hydrogen bromide as the sole side product. PPS obtained by this novel reaction is comparable with commercial PPS in molecular weights. This novel reaction was also applied to the

copolymerization of arylene dithiols with dibromo aromatic compounds. A mechanism for the novel polymerization reaction was proposed.

Sulfur containing high performance polymers may introduce the excellent properties related to PPS, such as excellent heat resistance, flame resistance, *etc.*. In Chapter 7, we synthesized a series of novel, amorphous poly(arylene thioether)s by the standard reaction of arylenedithiols with activated dihalocompounds in the presence of anhydrous potassium carbonate. These polymers have high glass transition temperatures and high thermal stabilities. They are soluble in common organic solvents and can be readily processed from solutions.

Although the reaction between arylene dithiols and activated dihalo compounds has been commonly used to prepare poly(arylene thioether)s, the availability of arylene dithiols is limited and they are unstable to oxidation. We have devised a novel one-pot polymerization reaction of bis(N,N'-dimethyl-S-carbamate)s with activated dihaloaromatic compounds in Chapter 8. This polymerization reaction was realized in the presence of a cesium carbonate and calcium carbonate mixture. Bis(N,N'-dimethyl-S-carbamate)s can be conveniently prepared from readily available bisphenols by the Newman-Kwart rearrangement reaction and can be easily purified. This novel polymerization reaction avoids the use of unstable, odorous, and difficult to purify arylene dithiols. This novel reaction opens a new door for synthesis of novel poly(arylene thioether)s as well as novel poly(arylene sulfone)s. A series of new high performance polymers, poly(arylene thioether)s, have been prepared by taking advantage of this novel polymerization reaction starting from 9,9'-bis(4-hydroxyphenyl)fluorene, 2,2'-bis(4-hydroxyphenyl)hexafluoropropane, and 1,2-dihydro-4-(4-hydroxyphenyl)(2*H*)phthalazin-1-one.

Cyclic oligomers have much lower melt viscosities compared with their high molecular weight linear polymers analogs. To solve the processing problem for high performance polymers related to the extremely high melt viscosities, two series of cyclic(arylene ether) oligomers have been synthesized and characterized. They are derived from 1,2-bis(4-fluorobenzoyl)-3,4,5,6-tetraphenylbenzene and bis(4-fluorophenyl)phenylphosphine oxide, respectively. A new strategy has been applied to synthesize cyclic(arylene ether) oligomers derived form 1,2-bis(4-fluorobenzoyl)-3,4,5,6-tetraphenylbenzene which is insoluble in DMF, a favorable solvent for the cyclization. The reactants were periodically added to the reaction vessel in portions in the solid state. Cyclic(arylene ether) oligomers undergo ring-opening polymerization to give high molecular weight polymers in the melt in the presence of a suitable initiator, such as potassium biphenoxide.

The last chapter of the thesis describes a series of novel highly fluorescent materials, isoindole containing polymers, which can potentially be used for fabricating light emitting diodes (LEDs). The synthesis of these polymers was achieved by treating the precursor polymers containing the 1,2-dibenzoylbenzene moiety with anilines in the presence of catalytic amount of *p*-toluenesulfonic acid at 200 °C. The resulting polymers were characterized by ^{1}H-NMR, DSC, TGA, UV-vis and fluorescence.

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Glossary of abbreviation and symbols

Å	Angstrom (1×10^{-8} cm)
λ_{max}	Maximum wavenumber
δ	Chemical shift
μL	Microliter
CHP	N-Cyclohexyl-2-pyrrolidinone
dL	Deciliter
DMAc	N,N'-Dimethylacetamide
DMF	N,N'-Dimethylformamide
DMSO	Dimethylsulfoxide
DMTA	Dynamic mechanical thermal analysis
DSC	Differential scanning calorimeter
EL	Electroluminescence
GPC	Gel permeation chromatography
HPLC	High performance liquid chromatography
IR	Infrared
LED	Light-emitting diode
MALDI-TOF-MS	Matrix assisted desorption ionization - time of flight - mass spectrometer
mol	Mole
M_w	Weight average molecular weight
M_n	Number average molecular weight
mp	Melting point
MS mass	Mass spectrum
nm	Nanometer
NMP	N-Methyl-2-pyrrolidinone
NMR	Nuclear magnetic resonance
PL	Photoluminescence
PPS	Poly(phenylene sulfide)
tan δ	Loss tangents
T_c	Crystallization temperature

T_g	Glass transition temperature
TGA/DTA	Thermogravimetric / differential thermal analysis
T_m	Crystalline melting temperature
TMA	Thermal mechanic analysis
TMEDA	N,N,N',N'-tetramethylethylenediamine
TMS	Tetramethyl silane
UV	Ultraviolet
WAXD	Wide-angle x-ray diffraction

Chapter 1. Introduction

1.1. High performance polymers

In his textbook, Odian defined the term *high performance polymer* as a polymer "that can be utilized at higher temperatures; that is, its mechanical strength and modulus, stability to various environments (chemical, solvent, UV, oxygen), and dimensional stability at higher temperatures match those of other polymers at lower temperatures".[1] Generally, high-performance polymers are considered to be materials containing high aromatic content and/or heterocyclic units. These materials may also contain some flexible linkages, such as -O-, -S-, -$(CH_3)_2$C-, -CO-, -SO_2-, *etc.*, which enable the materials be processable while at the same time they maintain good thermal and mechanic properties. Some representive classes of high performance polymers are poly(arylene ether)s (PAE), poly(imide)s, polybenzimidazoles and rigid rod or extended chain heterocyclic polymers. Research on high-performance polymers began in the late 1950s and early 1960s. Early examples are the discoveries of the oxidative coupling polymerization of 2,6-dimethylphenol[2,3], syntheses of high molecular weight poly(arylene ether)s by the nucleophilic substitution of activated aromatic halides[4], or by the Friedel-Crafts reactions.[5] High performance polymers are now extensively used in automotive and aircraft components, nonstick and decorative coatings, space vehicles, and missiles, electronic and microelectronic components, *etc.*.

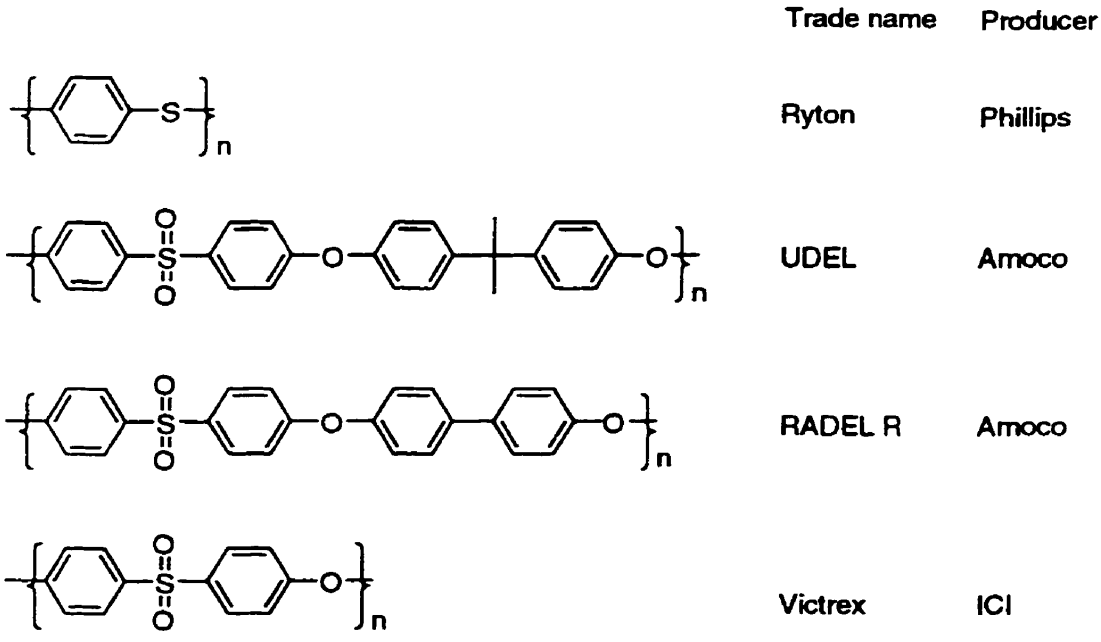
1.2 Nomenclature

We have been made an effort to use IUPAC nomenclature for the compounds and polymers. However, some terms which are more familiar to polymer scientists are used throughout this thesis, such as poly(phenylene sulfide) which is much more commonly used rather than poly(thiophenylene). In Chapter 1, a general term poly(arylene thioether) is used to refer an aromatic polymer containing a sulfur linkage in the main chain. However, in latter chapters, the term poly(thioarylene) is used to refer a polymer without an electron withdrawing group adjacent to the thioether linkage and the term poly(arylene thioether) is used to refer to a polymer prepared by a nucleophilic subsitution reaction, which means an electron withdrawing group is adjacent to the thioether linkage.

1.3. Important sulfur containing polymers

Among the family of high performance polymers, polymers containing sulfur in the main chains are very important members. Typical examples are shown in Scheme 1.1.

Poly(phenylene sulfide) (PPS) is a semicrystalline polymer with a glass transition temperature (T_g) around 85 °C and a melting point (T_m) around 285 °C. This material has an upper use temperature in the range of 200 - 240 °C. PPS is soluble only in aromatic hydrocarbons and chlorinated aromatic hydrocarbons at temperatures above 200 °C. Therefore, it has excellent chemical resistance. The inherent non-flammability, long term thermal stability, excellent affinity for a variety of fillers and its ability to be cross-linked at elevated tempeartures make PPS a very attractive material. Applications of PPS have been developed in electrical/electronic areas and mechanical areas, such as in coil forms, sockets, bolt yokes, motor brush holders, connectors, switches, integrated circuit and capacitor encapsulations, pump housings, impeller diffusers, pump vanes, valve components, heat shields, oil well valves, *etc.*.[6,7]



Scheme 1.1. Important high performance polymers containing sulfur in the main chains

Polysulfones possess very good mechanical properties and have excellent resistance to aqueous environments, including acids, bases, and oxidants.

Polysulfones are amorphous polymers with T_gs of 180 - 230 ℃ and they can be continuously used in the range of 150 - 200 ℃. Applications for polysulfones have been developed in microwave cookware, medical and biological equipment, eletronic components, and membranes for separations. The disadvantages of polysulfones are their poor resistance to organic chemicals and relatively low UV stability.

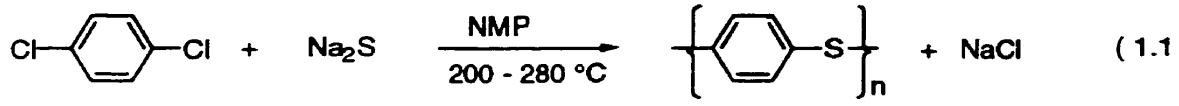
In addition to the high performance application area, sulfur containing polymers have played very importants roles in rubber industry. As early as 1929, Thiokol company (U. S. A.) marketed the first synthetic polysulfide rubber, Thiokol A, i.e., poly(ethylene tetrasulfide). The disadvantages of Thiokol A, i.e., difficulty in processing, inferior physical properties and a disagreeable odour, were soon overcome by Thiokol B, which was made from bis(2-chloroethyl)ether and sodium tetrasulfide. The present commercial products are of the poly(ethyl formal disulfide) type. Thiokol LP series of polymers are thiol-terminated liquid polysulfides, which can be compounded without heavy mixing equipment. Sulfur based elastomers have high resistance to the environmental degradation, good low temperature properties, low water vapor transmission, good adhesion to wood, metal, glass and concrete. They also have good resistance to solvents, water, acids and bases.[8,9]

1.4. Synthetic methods for poly(arylene thioether)s

1.4.1. Preparation of poly(arylene thioether)s by a nucleophilic substitution reaction.

Preparation of poly(arylene thioether)s from sodium sulfide and dihaloaromatic compounds.

The commercial processes used to prepare poly(arylene thioether)s are based on the so-called Phillips process (Equ. 1.1), which starts from a dihalocompound and sodium sulfide.[10] The polymerization reaction takes place in NMP at 200 - 280 ℃ under pressure. PPS produced by this process is a linear material containing 150 - 200 repeating units, giving a molecular weight in the range of 15,000 - 20,000. Several steps are involved in this process: (1) preparation of sodium sulfide from aquous sodium hydrosulfide and caustic in a polar solvent; (2) dehydration of the sodium sulfide; (3) polymerization of dichlorobenzene and sodium sulfide; (4) polymer recovery; (5) removing the salt by-product.



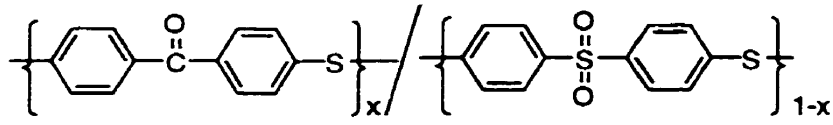
(1.1)

Kinetic studies have concluded that the polymerization reaction is a S_NR reaction.[11] However, the reaction is not a simple nucleophilic substition reaction by a sulfur anion. The solvent NMP plays a extremely important role. It functions as a catalytic reactant, transforming Na_2S into a soluble nucleophile. The empirical formula $Na_2S.NMP.H_2O$ or sodium 4-(N-methylamino)butanoate-NaSH have been proposed for the nucleophile.[11] Actually, in other solvents such as DMAc and DMF, no high molecular weight polymer could be obtained for non-activated dihalocompounds.

The major drawbacks of this process are the harsh reaction conditions and the production of large amount of salt by-product, which is hard to completely remove from the end products.

1.1

1.2

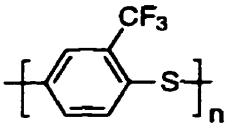


1.3

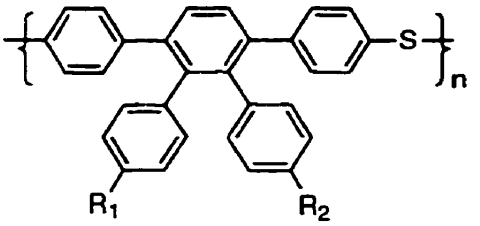
Other poly(arylene thioether)s have been prepared in a similar way. Poly(thiobiphenyl) (**1.1**) was prepared from 4,4'-difluorobiphenyl or 4,4'-dibromobiphenyl in NMP.[12] Polymer **1.1** is a highly crystalline polymer with a T_m of 445 °C. High molecular weight poly(thioether ketone) (**1.2**) was prepared by polymerization of 4,4'-difluorobenzophenone and sodium sulfide in N-cyclohexyl-2-pyrrolidinone (CHP) at 290 °C.[13] Polymer **1.2** with inherent viscosity of 0.95 was obtained in 0.5 h. This polymer has a T_g of 152 °C and a T_m of 335 °C. Attempted polymerization in diphenyl sulfone or sulfolane only resulted in low molecular weight oligomers.[14] However, in NMP, high molecular weight poly(thioether ketone) and poly(thioether sulfone) were obtained.[15,16] The random copoly(thioether

ketone/sulfone)s (**1.3**) were synthesized and characterized by Senn.[17] When the mole ratios of sulfone/ketone (S : K) > 25 : 75, the copolymers are amorphous. These materials form tough, creaseable films and exhibit a linear increase in T_g with the increase of sulfone content.

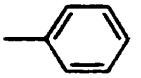
Relatively low molecular weight polymer **1.4** was also synthesized from sodium sulfide and dihaloaromatic compounds.[18] The polymer is soluble due to the trifluoromethyl substitutent. The T_g of this polymer is 98 °C. A series of substituted poly(thioether *p*-terphenyl)s (**1.5**) have been prepared by Kallitsis *et al.* from the corresponding dihalo compounds and sodium sulfide.[19] The polymers have T_gs ranging from 135 °C to 230 °C and they are amorphous and can be processed in solution.

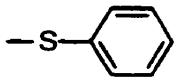


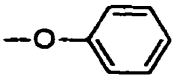
1.4



$R_1 = R_2 = H$

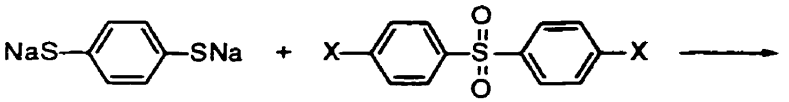
$R_1 = R_2 =$ 

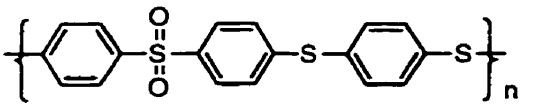
$R_1 = R_2 =$ 

$R_1 = R_2 =$ 

$R_1 = H, R_2 = OCH_3$

1.5





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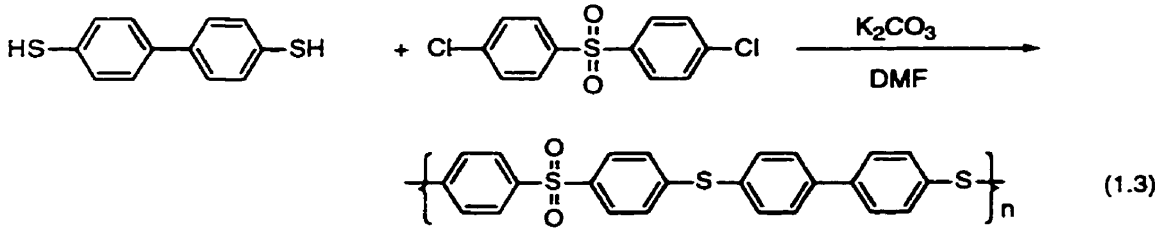
1.6

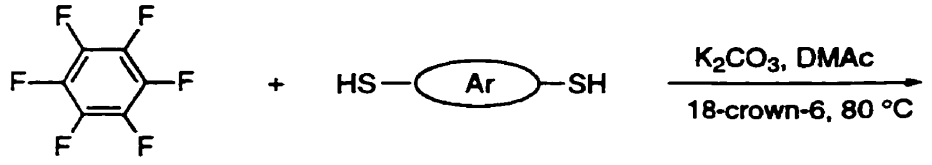


(1.3)

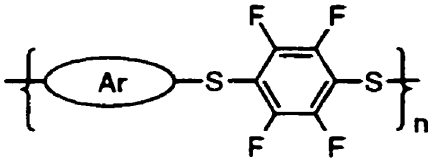
1.7

Preparation of poly(arylene thioether)s from arylene dithiols and dihaloaromatic compounds.

The polymerization reactions are generally carried out in a polar solvent, such as DMSO, DMF, and DMAc in the presence of a base. Dihalo aromatic compounds are generally activated by electron withdrawing groups. The first description of such a process was given by Kreuchunas,[20] who prepared a poly(thioether sulfone) (**1.6**) from bis(4-chlorophenyl)sulfone and alkaline *p*-benzenedithiolate. Baron *et al.* prepared the polymer **1.7** from 4,4'-biphenyldithiol and bis(4-chlorophenyl)sulfone in DMF in the presence of anhydrous K_2CO_3.[21]

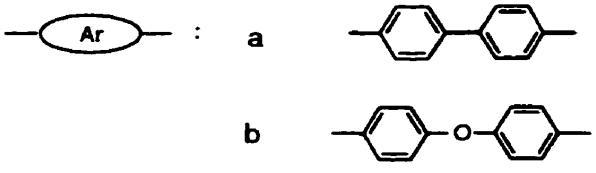


1.7 a-b

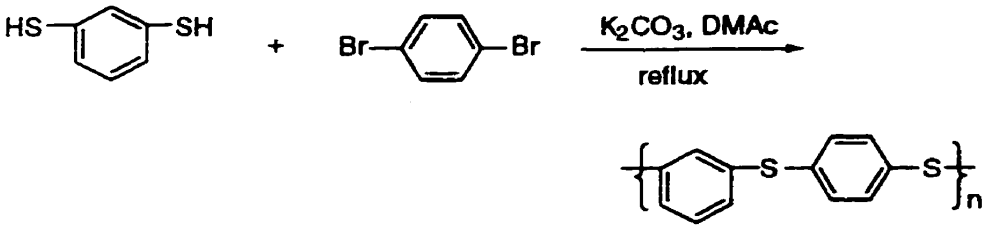


(1.4)

1.8 a-b

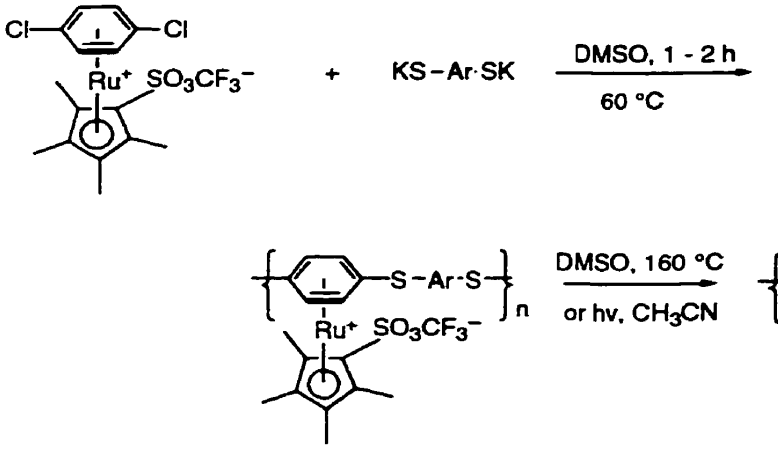


In the presence of a phase transfer catalyst, two fluorinated poly(thioether)s were prepared from arylene dithiols and fluorinated aromatic compounds (Equ. 1.4).[22] Hexafluorobenzene is activated by the strong electron withdrawing fluorine atoms. This process has the advantage that it can produce poly(arylene thioether)s which can not be prepared by normal reaction procedures, because of the low boiling points of the starting material hexafluorobenzene.[23]



(1.5)

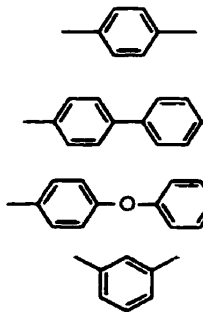
1.9



(1.6)

1.10 a-d **1.11 a-d**

Ar =



a

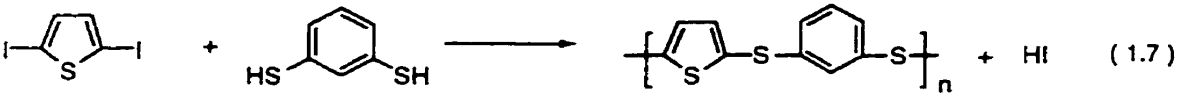
b

c

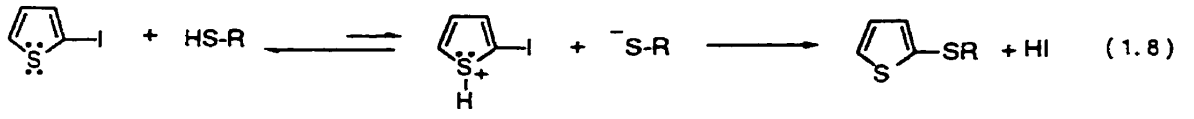
d

Non-activated dihalo compounds have also been used to prepare poly(thioether)s.[24] However, only low molecular weight oligomers were obtained (Equ. 1.5). Transition metals have been used to activate the nonactivated aromatic dihalides. A series of poly(thioether)s have been prepared from [Cp*Ru-(η^6-1,4-dichlorobenzene)]$^+$OTf$^-$ (OTf = SO_3CF_3) (**1.10**) with a stoichiometric ratio of the preformed dipotassium salts of arylene dithiols (Equ. 1.6).[25] The polymers **1.11a-d** were obtained after demetallation.

A very special case was reported by Lee and Hong.[26] They prepared poly(2,5-thiophenyl thioether) by simply mixing 2,5-diiodothiophene and arylenedithiols with absence of solvent, base or catalyst (Equ. 1.7). The proposed mechanism is shown in Equ. 1.8.

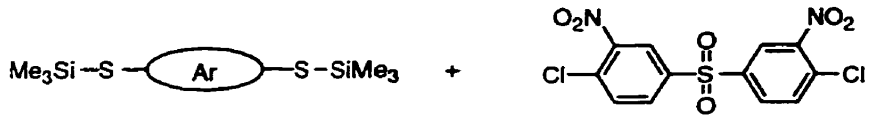


(1.7)

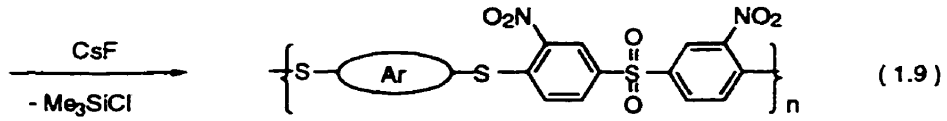


(1.8)

The thiol group is not oxidatively stable and thiols generally have disagreeable odors. Their purification and handling are generally very tedious. Two methods have been developed to try to solve these problems. Kricheldorf *et al.*[27] and Hara *et al.*[28] reported the synthesis of poly(arylene thioether)s from S,S'-bis(trimethylsilyl)-substituted arylene dithiols and activated aromatic dihalides in the presenc of catalytic amounts of cesium fluoride. The polymerization reaction was carried out in the melt and the sole side product, trimethyl silyl chloride was removed by distillation. Therefore, clean polymers are obtained at the end of the reaction. However, the monomers are moisture sensitive and the reactivities are very low, which makes the polymerization process useful only for special cases.

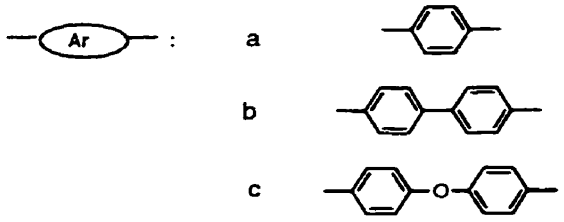


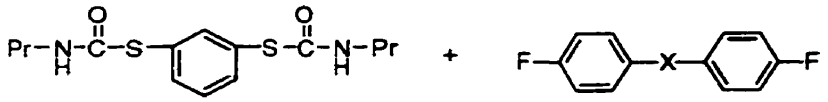
1.12 a-c



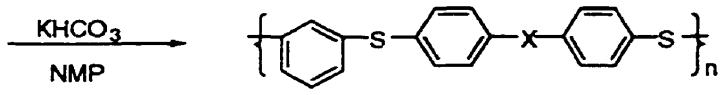
(1.9)

1.13 a-c



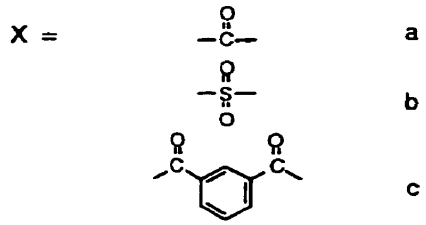


1.14 **1.15 a-c**



(1. 10)

1.16 a-c



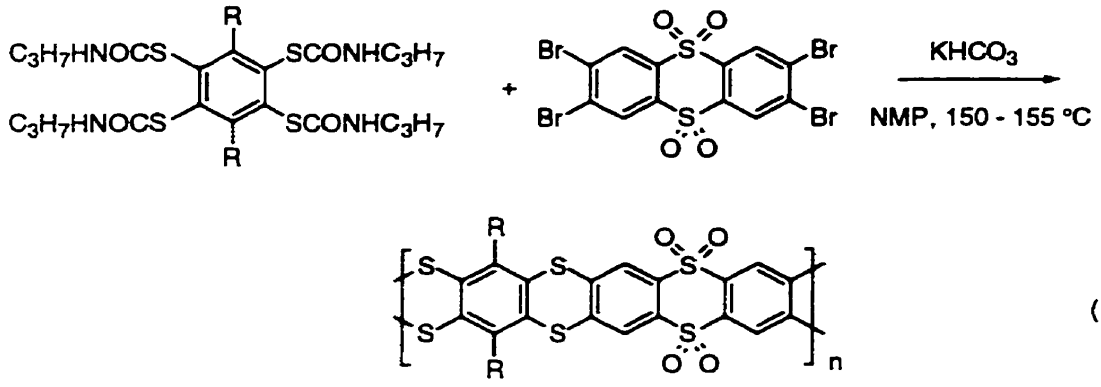
a

b

c

A much more convenient and practical process to prepare poly(arylene thioether)s was developed by Wang and Hay in 1992.[29] It was found that bis(N-propyl-S-carbamate) substituted arylene dithiols can be efficiently cleaved in NMP in the presence of $KHCO_3$ at 150 °C to form dithiolates. High molecular weight polymers were obtained in 2 hours (Equ. 1.10). Arylene dithiols can be easily transformed into bis(N-propyl-S-carbamate)s by reaction with propyl isocyanate. The bis(N-propyl-S-

carbamate)s can be easily purified by recrystallization and are stable to oxidants. This novel polymerization reaction has been utilized to synthesize polymers with ribbon topology structure (Equ. 1.11).[30]



(1.11)

Both the silyl and N-propyl-S-carbamate masked arylene dithiols have to be prepared from the existing arylene dithiols, so that the problem of limited availability and instability towards oxidation and disagreeable odor are not avoided.

1.4.2. Preparation of poly(arylene thioether)s by electrophilic substitution reactions.

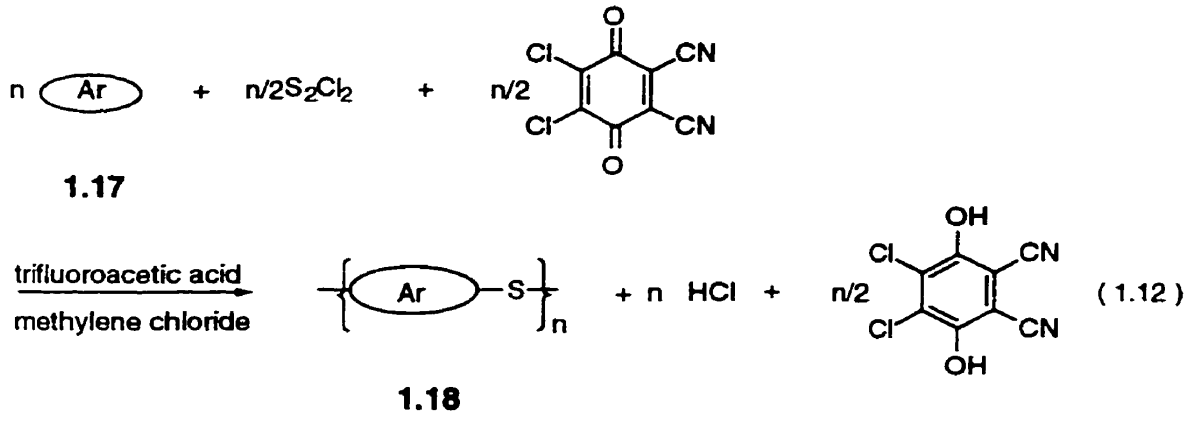
Preparation of poly(arylene thioether)s from sulfur and aromatic hydrocarbons.

As early as 1888, Friedel and Crafts reported that sulfur reacts with benzene to give several products in the presence of $AlCl_3$.[31] Genvresse obtained oligomeric materials by studying the same reaction.[32] In 1984, Cleary reexamined the reaction.[33] He performed the reaction in 1,2,4-trichlorobenzene and found that the yield of the polymer increased as the amount of sulfur added was increased. Polymers with molecular weights in the range of 2900 - 4300 (DP = 23 - 35) were obtained. The polymer chains contain large amount of the thianthrene structure. Because $AlCl_3$ catalyzes both polymerization and degradation reactions, this process is not suitable to prepare high molecular weight polymers.

Preparation of poly(arylene thioether)s from SCl_2 or S_2Cl_2.

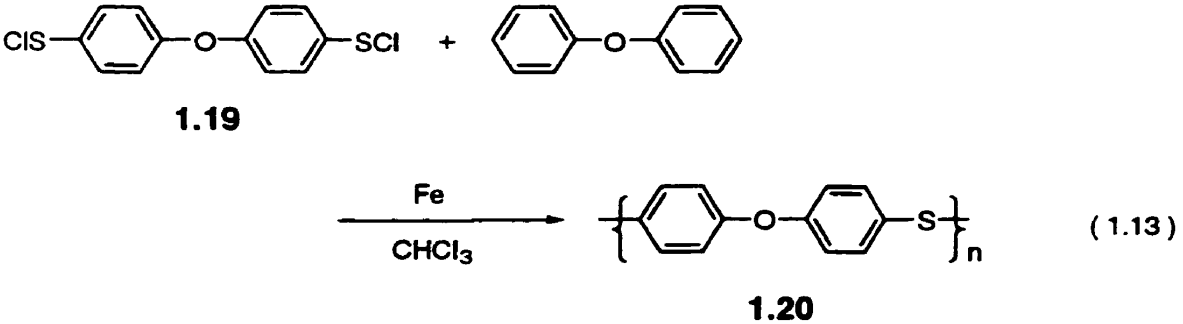
SCl_2 or S_2Cl_2 reacts with diphenyl ether in chloroform in the presence of catalytic amounts of iron to form poly(arylene thioether)s.[34] The former gave

crystalline polymers, while the latter gave amorphous polymers due to the presence of disulfide linkages. The inherent viscosities of these polymers are in the range of 0.09 - 0.10 dL/g. Bi, Sn, Sb or $FeCl_3$ have also been found to catalyze the reaction.[34-36] In all cases, the polymers obtained are low molecular weight oligomers and are often contaminated with disulfide or thianthrene groups. Most recently, Yamamoto *et al.* reported that aromatic hydrocarbons react with S_2Cl_2 to form sulfide bonds preferentially in the presence of large amounts of strong acid and an equimolar amount of an oxidizing agent, such as 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ), or a catalytic amount of vanadyl compounds (Equ. 1.12).[37,38] Relatively high molecular weight polymers were obtained from monomers containing aliphatic substituents.



1.17 **1.18** (1.12)

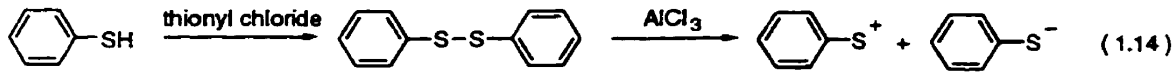
A related method is the condensation of bis(sulfenyl chloride)s with aromatic hydrocarbons.[39] Low molecular weight polymer **1.20** was obtained by reaction of **1.19** with diphenyl ether in chloroform in the presence of an iron catalyst (Equ. 1.13).



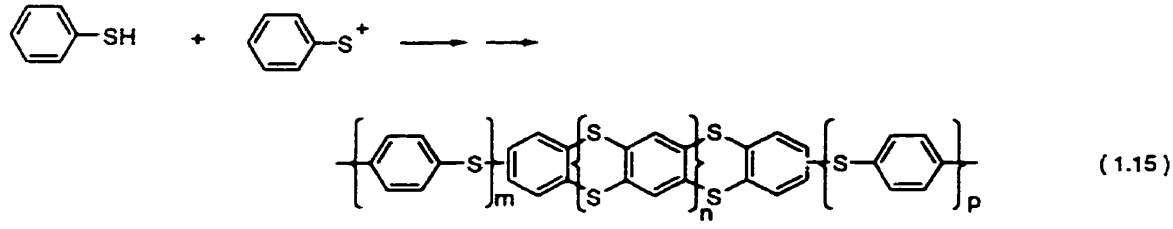
1.19 **1.20** (1.13)

Preparation of poly(arylene thioether)s from arylthiols or bisaryldisulfides.

Reaction of benzenethiol with thionyl chloride in the presence of a Lewis acid, such as $AlCl_3$, leads to insoluble polymers containing thianthracene bonds (Equ. 1.14-15).[40,41]



(1.14)



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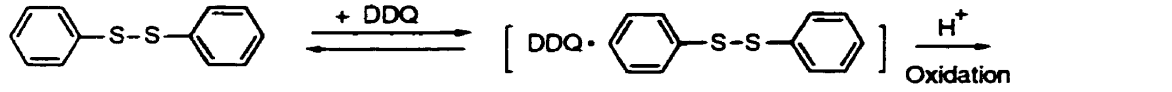
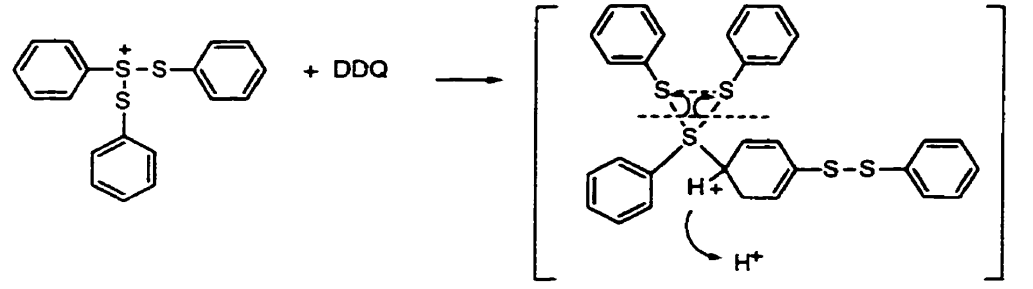




(1.16)

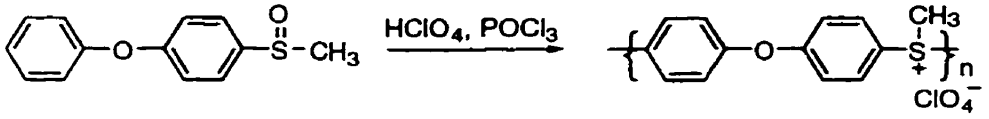
In the presence of an oxidant and large amounts of a strong acid, such as trifluoroacetic acid, diphenyl disulfide or benzenethiol undergoes a polymerization reaction forming poly(phenylene sulfide).[42-45] The reaction was generally carried out in methylene chloride at room temperature. DDQ, a strong Lewis acid such as $SbCl_5$, and oxygen in the presence of an oxovandium catalyst have been used as oxidants.

The phenylbis(phenylthio)sulfonium cation was suggested as the reaction intermediate (Equ. 1.16).[42-46]

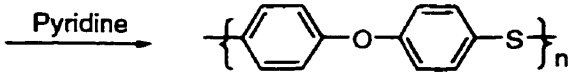
Because the reactions were carried out at room temperature in methylene chloride and PPS is highly insoluble, oligomeric PPS precipitated out of the solution before high molecular weights were obtained. Relatively higher molecular weight polymers were obtained in the synthesis of amorphous poly(arylene thioether)s.[45,47]

Preparation of poly(arylene thioether)s from alkylsulfinyl aromatics or alkyl thioaromatics.

Poly(arylene thioether)s have been prepared from soluble precursors, poly(arylene sulfonium salt)s. Fujisawa *et al.* found that high molecular weight poly(alkyl 4-phenoxyphenylsulfonium salt) (**1.21**) could be obtained by self polymerization of alkylsulfinyl-4-phenoxybenzene in a mixture of 70% perchloric acid and phosphorous oxychloride.[48] The soluble polysulfonium salt can be dealkylated on treatment with boiling pyridine to afford the poly(arylene thioether)s (Equ. 1.17).



1.22

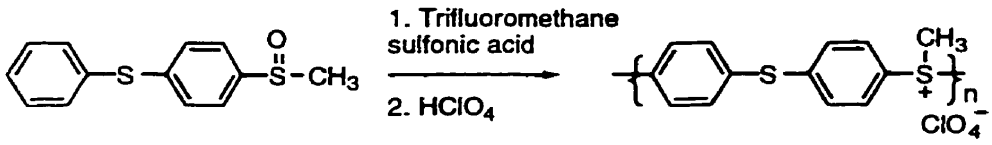


(1.17)

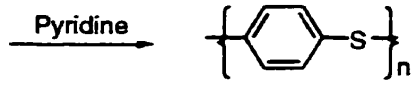
1.23

This polymerization reaction was further extensively studied by Tsuchida *et al.*. High molecular weight PPS was obtained from self polymerization of methyl sulfinyl-4-thiophenoxy benzene in trifluoromethane sulfonic acid followed by dealkylation in pyridine (Equ. 1.18).[44,49] In the presence of an oxidant, alkylthio aromatics underwent oxidative polymerization to form polysulfonium salts directly.[50-52]

The same reaction has also be extended to AA, BB type monomers. Poly(arylene sulfonium salt)s have been prepared by copolymerization of aromatic compounds and methyl sulfinic acid in trifluoromethanesulfonic acid.[53,54]



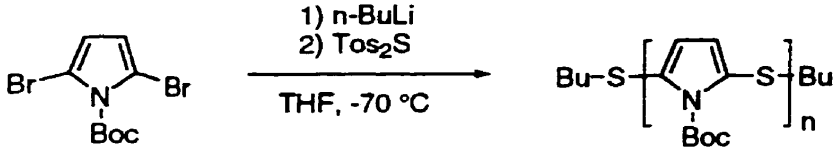
1.24



(1.18)

Preparation of poly(arylene thioether)s from bis(phenylsulfonyl)-sulfide

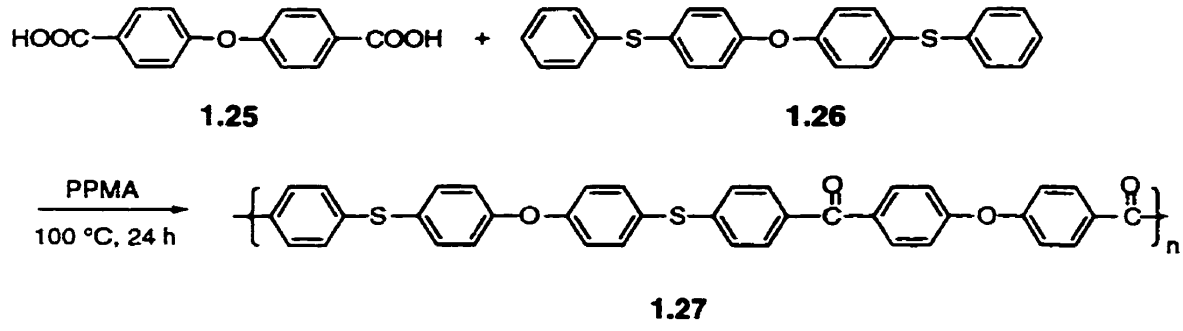
Recently, Groenendaal *et al.* reported the synthesis of N-*t*-Boc protected pyrrole-sulfur oligomers *via* a two step reaction, starting from N-*t*-Boc-2,5-dibromopyrrole.[55] This compound was first lithiated at the α-positions using *n*-BuLi in THF at -70 °C, then an equivalent amount of bis(phenylsulfonyl)sulfide (Tos_2S) was added (Equ. 1.19).



(1.19)

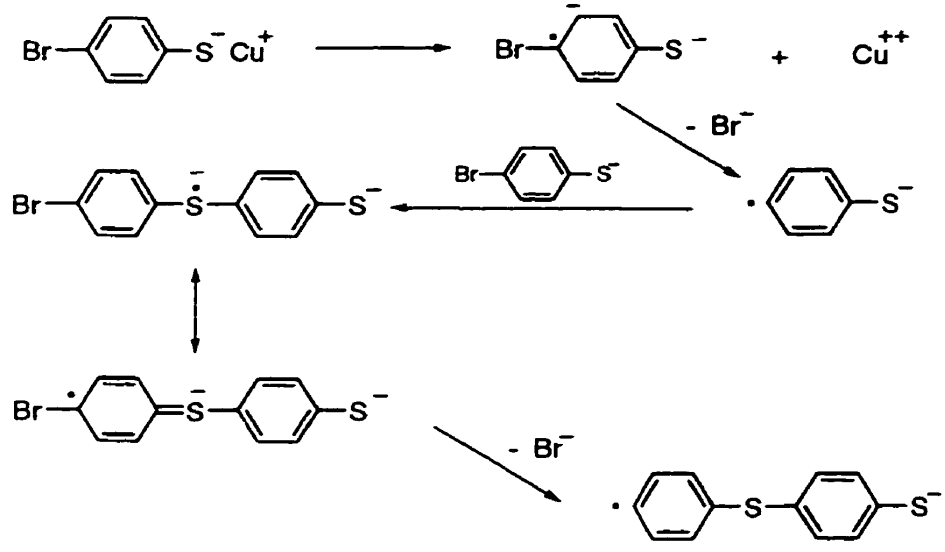
Preparation of poly(arylene thioether)s from aromatic thioethers by an electrophilic substitution reaction.

Theoretically speaking, poly(arylene thioether)s can be prepared from preformed aryl thioethers by several different polymerization reactions. Ueda *et al.* prepared a series of poly(thioether ketone)s by the direct polycondensation of aromatic dicarboxylic acids with aryl thioethers using Eaton's reagent, phosphorous pentoxide / methanesulfonic acid (1 : 10), as a condensing agent and solvent (Equ. 1.20).[56,57] One major drawback of this method is the use of large amounts of strong acids.

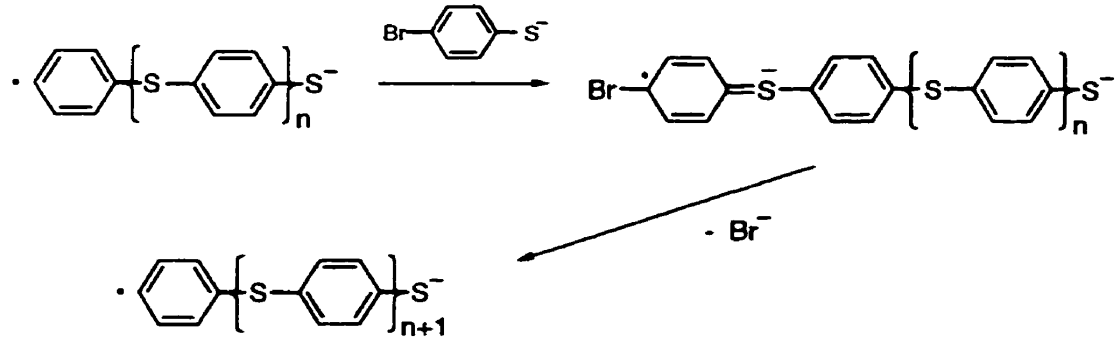


(1.20)

Initiation:



Propagation:

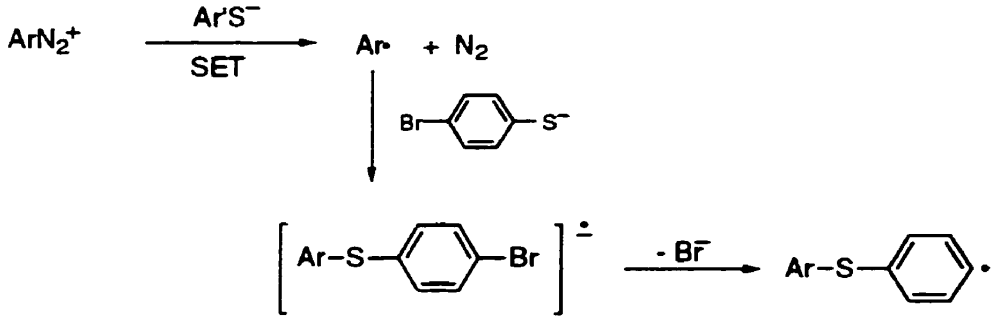


Scheme 1.2. $S_{RN}1$ - type mechanism for the polymerization of copper(I) 4-bromobenzenethiolate

1.4.3. Preparation of poly(arylene thioether)s by a single-electron transfer process.

Lenz *et al.* first prepared PPS from the self-condensation of 4-bromobenzenethiolate salts in pyridine under pressure.[58] This reaction was further thoroughly studied by Lovell *et al.*.[59-65] and a series of poly(arylene thioether)s including copolymers were prepared from the copper(I) bromoarylenethiolate in quinoline solution. The polymerization mechanism was first explained as a nucleophilic substitution mechanism.[58] However, the following observations led to the establishment of a $S_{RN}1$ type mechanism.[59,61] The IR spectra of the PPS formed show evidence only of 1,4-phenylene sulfide repeat units. Relatively high molecular weight PPS is formed at low monomer conversions for a condensation polymerization reaction (i.e. 70 -90%). The trends in monomer reactivity are for the halogen I > Br > Cl, F and for the metal ion $Cu^+ > Li^+ > Na^+ > K^+$. The proposed mechanism is shown in Scheme 1.2.

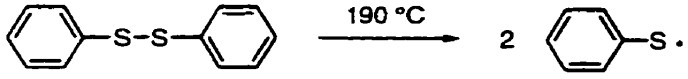
The polymerization of 4-bromobenzenethiolate salts has also been realized in DMSO at room temperature using catalytic amounts of a diazonium salt via a single electron transfer process (Scheme 1.3).[66] Since the reactions were carried out at room temperature and PPS is highly insoluble, it is not surprising that only very low molecular weight oligomers (DP = ~ 9) were obtained.



Scheme 1.3. Polymerization of sodium 4-bromobenzenethilate initiated by diazonium salt

1.4.4. Preparation of poly(arylene thioether)s by a free-radical substitution reaction.

Benati *et al.* has established that arylthio radicals replace the halogen atom in chloro-, bromo, and iodobenznzene at 150 - 190 °C *via* an *ipso*-substitution reaction (Equ. 1.21 - 22).[67] In the late 1980's, researchers at Eastman Chemical Company also studied this type of reaction. They prepared a series of poly(arylene thioether)s, including PPS, from melt copolymerization of arylene diiodides with elemental sulfur.[68-72] The polymerization reactions were carried out at 230 - 240 °C under vacuum (Equ. 1.22). The by-product iodine was recycled and used to prepare the arylene diiodide starting materials.[73] However, the poly(arylene thioether)s obtained are always contaminated by small amounts of disulfide linkages and a method for removal of these linkages has been patented.[74]



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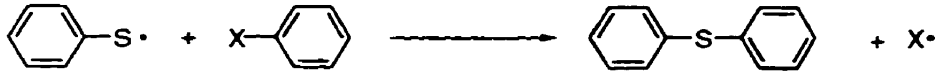

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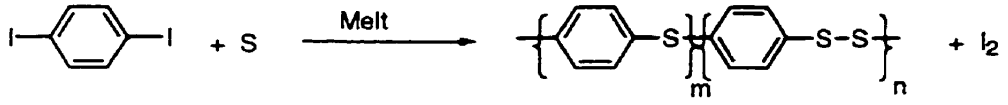

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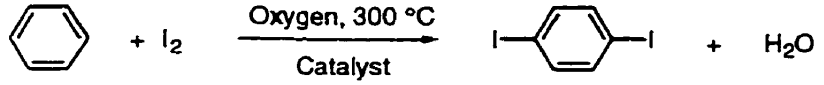
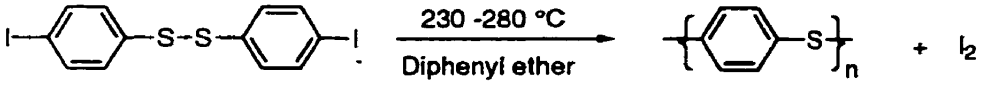


(1.23)

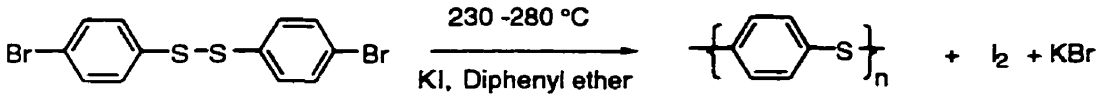
Later, linear high molecular weight PPS polymers were prepared from bis(4-iodophenyl)disulfide in diphenyl ether solution at 230 - 280 °C (Equ. 1.24).[75] PPS obtained using this method after annealing had a T_m of 313 °C.[76] The polymerization reaction has also been extended to prepare naphthalene containing polymers.[77]



(1.24)

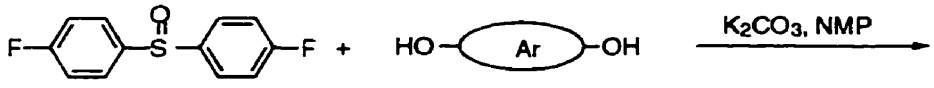
Although it has been reported that bis(4-bromophenyl)disulfide was recovered by heated at refluxing in quinoline solution because of no reaction,[60] high molecular

weight poly(arylene thioether)s were obtained from bis(4-bromophenyl)disulfide in diphenyl ether solution in the presence of the reducing agent, potassium iodide (Equ. 1.25).[77,78] In this polymerization process, KI serves as reducing agent and the bromine radicals are reduced to unreactive bromide anions, while at the same time the thiyl radicals are not affected.

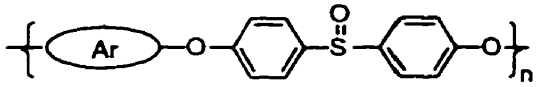


(1.25)

1.4.5. Preparation of poly(arylene thioether)s by the reduction of polysulfoxides.

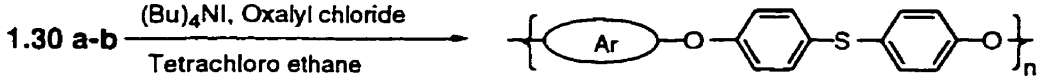


1.28 **1.29 a-b**



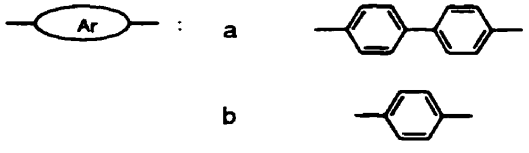
(1.26)

1.30 a-b



(1.27)

1.31 a-b



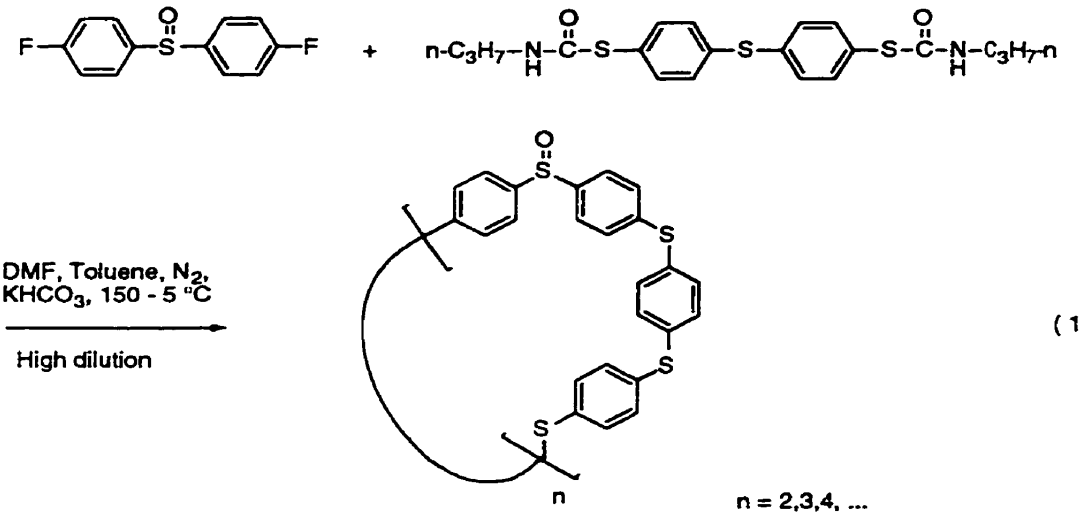
Poly(arylene thioether)s have also been synthesized by the reduction of poly(arylene sulfoxide)s, which were prepared from bis(4-fluorophenyl)sulfoxide by a conventional nucleophilic substitution reaction.[79-81] Tetrabutyl ammonium iodide and

oxalyl chloride were used together as the reducing agent (Equ. 1.26-27). This process has been used to prepare high molecular weight semi-crystalline polymers.

1.4.6. Preparation of poly(arylene thioether)s from a ring-opening polymerization reaction.

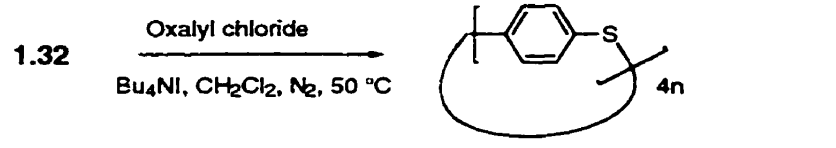
Recently, extensive efforts have been devoted to the synthesis of cyclic oligomers as precursors of high molecular weight polymers. The cyclic precursors have lower melt viscosities which facilitate the processing. In contrast, linear high molecular weight polymers have very high viscosities and are very difficult to process.[82] There is a significant advantage in preparing highly crystalline as well as highly insoluble polymers from cyclic oligomers, since cyclic precursors generally have much better solubility and are much easier to purify. Different types of cyclic oligomers including cyclic(arylene carbonate)s,[83-89] cyclic(arylene ester)s,[90,91] cyclic(arylene amide)s,[92,93] cyclic(ether sulfone)s,[94-98] cyclic(ether imide)s,[99] cyclic(ether ketone)s[95,100]and cyclic(arylene formal)s,[101] have been prepared and studied.

PPS cyclic oligomers have been isolated in small quantities from the commercial polymerization reaction mixtures.[102] A cyclic(phenylene sulfide) hexamer was isolated by the reaction between 1,4-dichlorobenzene and sodium sulfide.[103] PPS cyclic oligomers mixtures with different repeating units were prepared by the same reaction between 1,4-dichlorobenzene and sodium sulfide in NMP.[104] Wang and Hay prepared PPS cyclic oligomers from the precursor containing sulfoxide oligomers by reducing the sulfoxide bonds to thioether bonds (Equ. 1.28).[105] From the cyclic sulfoxide oligomers, a series of cyclic(arylene ether ether thioether) oligomers have also been synthesized. These cyclic(thioether)s undergo a ring-opening polymerization reaction to give high molecular weight polymers in the presence of an initiator, such as a phenoxide anion,[99] a cation[106] or a free radical.[107,108]



(1.28)

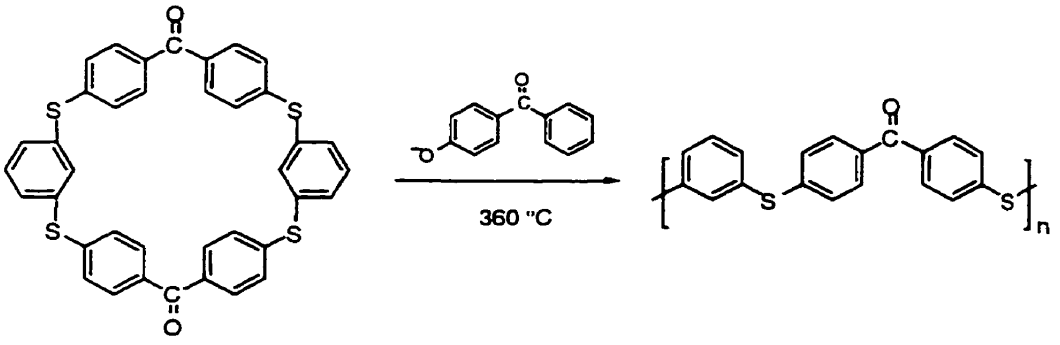
1.32



(1.29)

1.33

Recently, Colquhoun *et al.* reported that cyclic dimer **1.34** was formed as the major product by a nucleophilic condensation reaction between 1,3-benzenedithiol and 4,4'-difluorobenzophenone under high dilution conditions.[109] Cyclic dimer **1.34** underwent rapid anionic ring-opening polymerization in the melt (330 - 360 °C), affording a linear, high molecular weight poly(arylene thioether ketone) (Equ. 1.30).

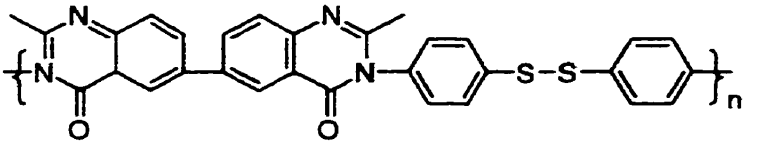


(1.30)

1.34 **1.35**

1.5. Syntheses of poly(arylene disulfide)s

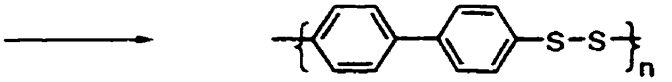
Little attention has been paid to the study of poly(arylene disulfide)s. Poly(arylene disulfide)s are generally insoluble in common organic solvents, such as chloroform, THF, NMP, *etc.*. Ghafoor *et al.* synthesized a polyquinazolone (**1.36**) containing a disulfide group from bis(4-aminophenyl)disulfide.[110] Polymer **1.36** showed increased ductility and decreased hardness upon curing due to the presence of the flexible disulfide linkage.



1.36

Bis(4-hydroxyphenyl)sulfone treated with S_2Cl_2 forms an hydroxy functionalized poly(arylene disulfide).[111] Several poly(arylene disulfide)s, including poly(biphenylene disulfide), have been synthesized from difunctional sulphenyl chlorides and dithiols (Equ. 1.31).[112] NMR and molecular weight data are not available for these materials because they are not soluble in common solvents.

1.37 **1.38**

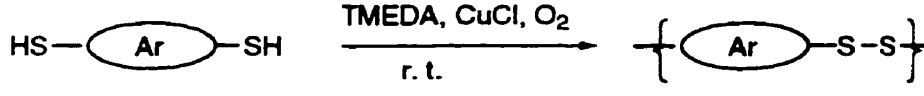


(1.31)

1.39

Iodine and DMSO have been commonly used as the oxidizing agents to prepare poly(arylene disulfide)s from the corresponding arylene dithiols. Poly(*m*-phenylene disulfide) was prepared from dithioresorcinol by oxidation with DMSO.[113] The number average molecular weight of the polymer obtained was 880 (DP *ca.* 6) and intrinsic viscosity in NMP at 30 °C was 0.11 dL/g. The oligomers were further chemically modified by chlorosulfonic acid and showed a conductivity of 1 x 10^{-5} S cm^{-1}. Using oxidative coupling with oxygen catalyzed by copper salts and an amine,

Hay was able to prepare a series of poly(arylene disulfide)s which were not soluble in common organic solvents, and which were not fully characterized (Equ. 1.32).[114]



(1.32)

1.6. Strategy and goals

Developing new polymerization reactions or new processes and synthesizing new materials with special properties are two of the major tasks of polymer chemists. As a training process for a polymer chemist, this thesis is devoted to exploring some new polymerization reactions or processes and preparing some new materials, which are briefly described here and will be described in detail in later chapters.

1. A series of cyclic(arylene disulfide) oligomers were synthesized by the oxidation of arylenedithiols with oxygen in the presence of a copper-amine catalyst under high dilution conditions.

2. The free-radical ring-opening polymerization of cyclic(arylene disulfide)s provides a novel process to prepare high molecular weight poly(arylene disulfide)s.

3. The copolymerization reactions between diiodo- or dibromoaromatic compounds affords a novel way to prepare high molecular weight PPS and poly(arylene thioether)s.

4. Self polymerization of 4-bromobenzenethiol in the presence of a free radical initiator affords another novel way to prepare high molecular weight PPS. HBr is the sole by-product of this reaction. This novel polymerization has also been extended to the co-polymerization reactions between arylene dithiols and dibromo aromatic compounds.

5. The novel free radical copolymerization reaction between cyclic(arylene disulfide) oligomers and elemental sulfur provides a novel process to polysulfide rubbers.

6. A one-pot polymerization reaction between bis(N,N'-dimethyl-S-carbamate)s and activated dihaloaromatic compounds was developed. Bis(N'N'-dimethyl-S-carbamate)s can be conveniently prepared from corresponding dihydroxy compounds via the Newman-Kwart rearrangement reaction. This novel polymerization reaction greatly facilitates the preparation of poly(arylene thioether)s.

7. The synthesis and ring-opening polymerization of a new series of cyclic(arylene ether)s were also studied.

8. Highly phenylated N-isoindoles were synthesized and a series of highly phenylated N-isoindole containing polymers were prepared, which can be potentially used as electroluminescent materials.

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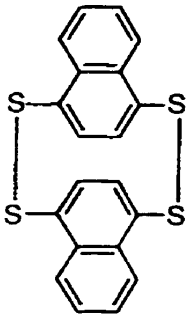
Chapter 2. Synthesis and Characterization of Cyclic(arylene disulfide) Oligomers

2.1. Introduction

Although the first cyclic(arylene disulfide) **2.1**, reported 40 years ago,[1] was synthesized with an unspecified yield from oxidation of 1,4-naphthalenedithiol with alkaline ferricyanide, only a few other cyclic(arylene disulfide)s have been reported since then. In 1976, Wong and Marvel synthesized a cyclic trimer **2.2** in 30% yield by oxidation of 1,4-dimercaptobenzene with iodine in ethanol and studied its application as a cross-linking agent.[2] Aimed at the synthesis of some novel complexing cyclics, Raasch was able to prepare a macrocyclic tetradisulfide **2.3** in 89% yield by using DMSO as oxidizing agent.[3] Cyclic(arylene disulfide)s **2.4-7** have been synthesized by using iodine as oxidizing agent,[4-6] and the structure of **2.7** has been confirmed by X-ray analysis.[6] The drive for the synthesis of most of these cyclics has been to study their structural geometry and their potential for complexation. Recently, extensive efforts have been devoted to the synthesis of cyclic oligomers for precursors of high molecular weight polymers,[7-26] since cyclic precursors have lower melt viscosities which facilitate the processing. Although aliphatic poly(disulfide)s have long been prepared from cyclic(aliphatic disulfide)s,[27] there has been little work carried out on the synthesis of poly(arylene disulfide)s from cyclic(arylene disulfide)s.[28] The poly(arylene disulfide)s have been studied to a limited extent due to their insolubilities in common organic solvents.[29-32]

Disulfide-disulfide interchange is relatively slow at temperatures below 150 ℃ or in the absence of UV light. Trace amounts of sulfur, mercaptides or alkaline agents capable of generating mercaptides by reaction with disulfide bonds catalyze the exchange reaction at moderate temperatures.[33] At high temperatures, the exchange reaction between disulfide bonds is much faster. Therefore, it is anticipated that cyclic(arylene disulfide)s would ring open and form high molecular weight polymers at high temperatures without adding any catalyst. Since cyclic(arylene disulfide) oligomers are readily soluble in organic solvents and can be easily purified, preparing poly(arylene disulfide)s from cyclic(arylene disulfide) oligomers could be a practical way to apply poly(arylene disulfide)s in coatings, sealants, etc.. Furthermore, cyclic(arylene disulfide) oligomers could be potentially applied as cross-linking

reagents. In 1991, Wang and Hay reported that poly(*p*-phenylene sulfide) (PPS) can be prepared by heating 4,4'-diiodophenyl disulfide.[34,35] Cyclic(arylene disulfide) oligomers are also potentially very useful intermediates for the synthesis of aromatic polysulfides by reacting with diiodo or dibromo compounds.



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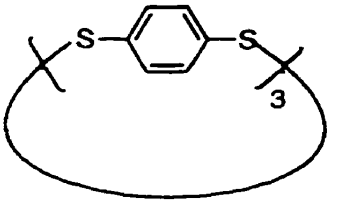

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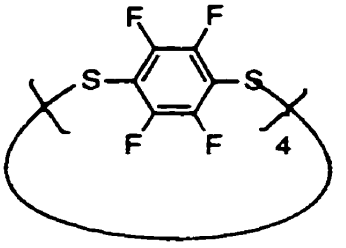
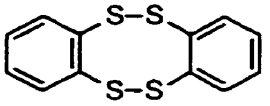


2.3



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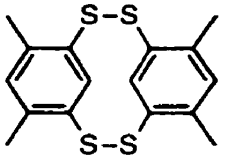

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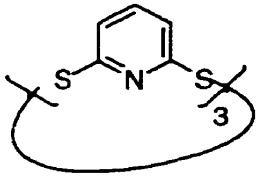
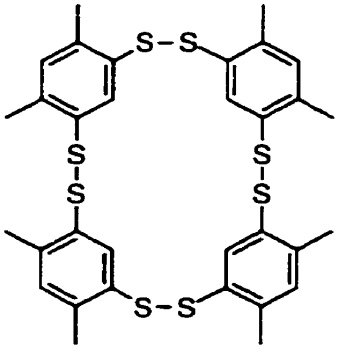


2.6



2.7

2.2. Strategy and goals

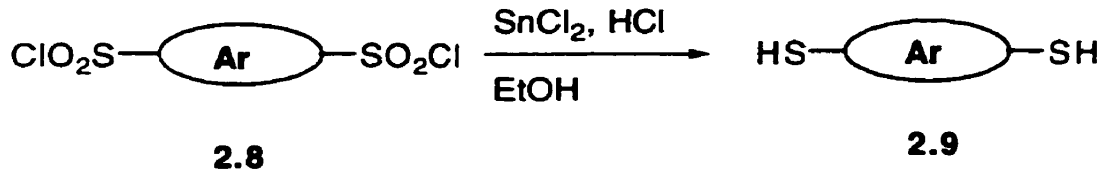
In this chapter, a series of aryldithiols were prepared using different synthetic techniques. These dithiol compounds were subjected to an oxidation reaction with oxygen under high dilution conditions in the presence of a copper-amine catalyst. A series of cyclic(arylene disulfide) oligomers were synthesized and characterized by gradient HPLC, GPC, MALDI-TOF-MS, DSC and DTA techniques. Subsequent

chapters will describe the details of studies on the ring-opening polymerization reaction of cyclic(arylene disulfide) oligomers and the synthesis of polysulfides from cyclic(arylene disulfide) oligomers.

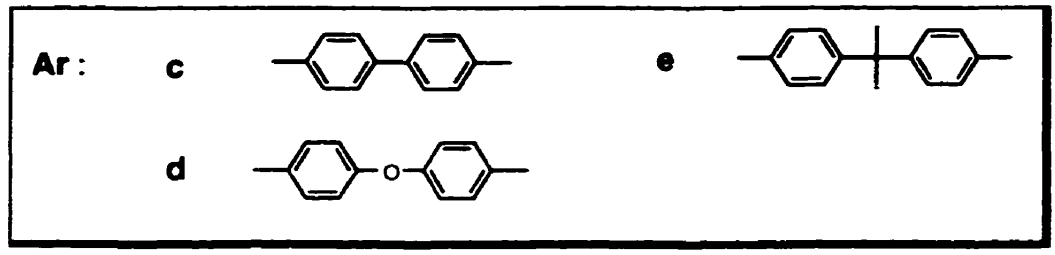
2.3. Synthesis of arylene dithiol compounds.

Three different methodologies have been used to prepare aryldithiols, as illustrated in Schemes 2.1-3.

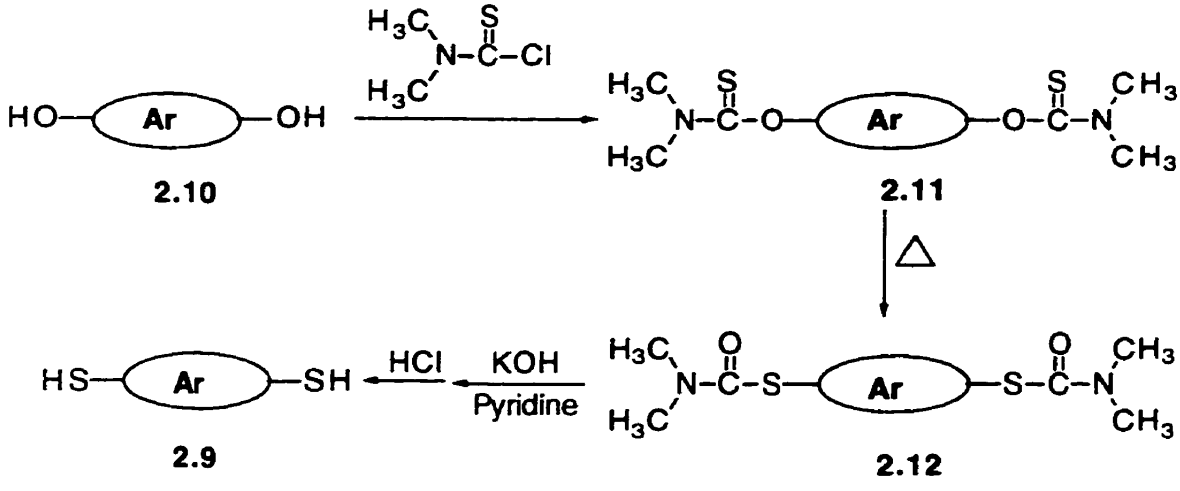
Compound **2.9e** was synthesized from 2,2'-diphenylpropane. Chlorosulfonation of 2,2'-diphenyl propane gave disubstituted products. The crude product precipitated out from water contained a large amount of trapped water which was very difficult to remove by heating. However, extracting the product with toluene and evaporation of solvent gave a material pure enough for the next reaction step. For the best results, the crude disulfonylchloride should be recrystallized from hexane or acetic acid. The ketone, sulfone, or phosphine oxide containing aryldithiols could be synthesized from the corresponding dichloro- or difluoro- compounds and sodium hydrogen sulfide in DMF. This is a very easy synthesis that can be readily carried out on a 100 g scale in the laboratory. Monomers **2.9h-2.9o**, which contain either ketone, sulfone or phosphine oxide groups, are easily oxidized by air to form disulfide compounds at 80 °C. These disulfides can not be dissolved in 5% NaOH solution. In contrast, **2.9a** can be dried at 100 °C for very long time with little disulfide formation. The presence of disulfide in aryldithiols can be easily detected by ^{1}H-NMR. If there is any disulfide present, the proton signals of the benzene ring connecting to disulfide linkage shift down field. To avoid the oxidation, all of the aryldithiols were dried at room temperature under vacuum. For the present purpose, the presence of small amounts of disulfide does not interfere with the formation of cyclic oligomers. Compounds **2.9h** and **2.9n** have been made by other methods.[36,37] The phenyl phosphine oxide and ketone containing dithiols, except **2.9h**, are new compounds.

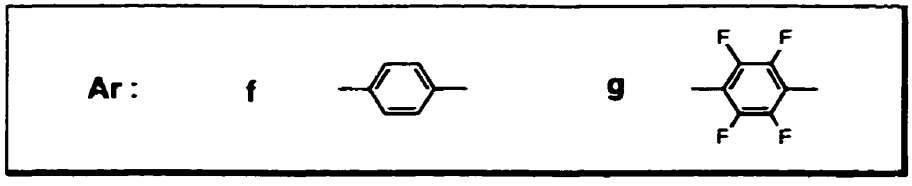


2.8 **2.9**

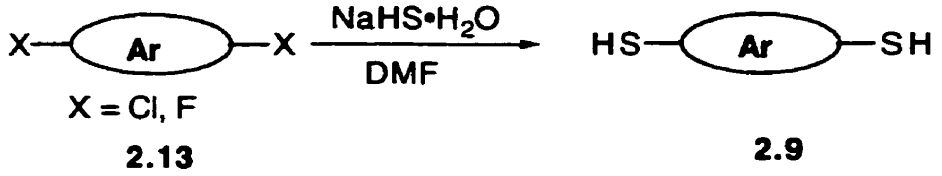


Scheme 2.1. Preparation of aryldithiols from aryldisulfonyl chlorides.

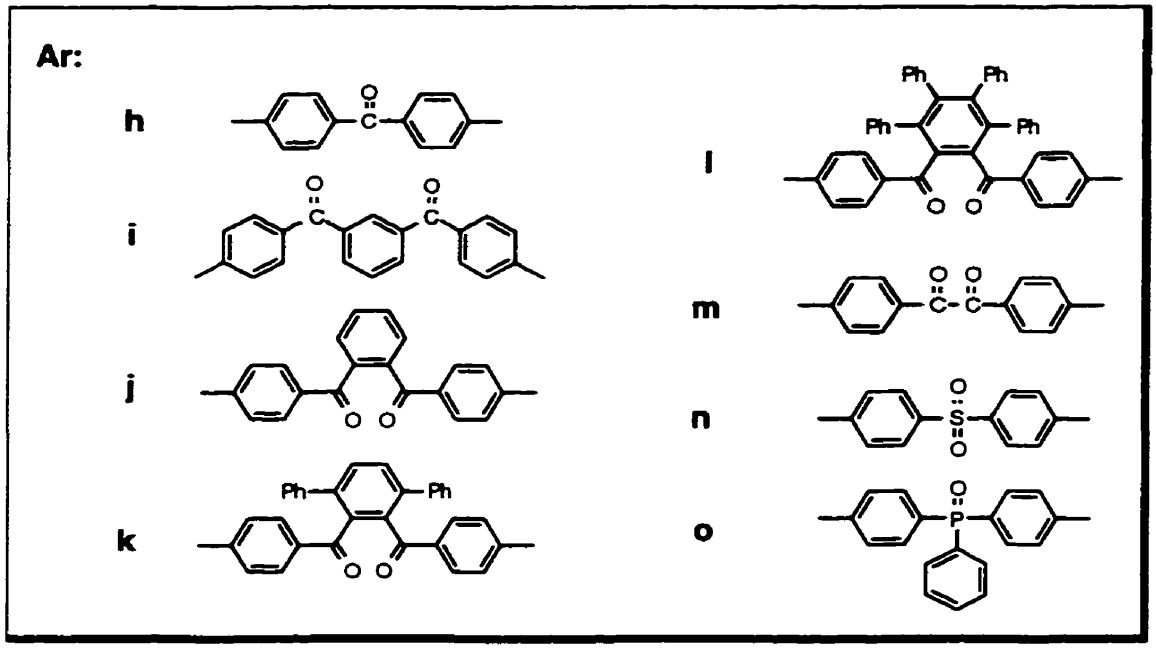




Scheme 2.2. Preparation of aryldithiols from dihydroxy compounds



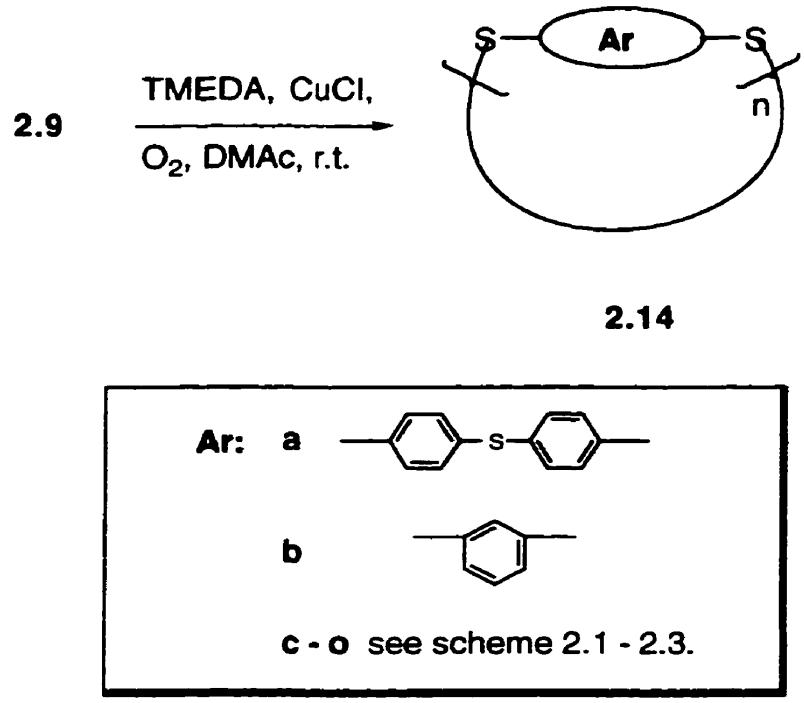
2.13 **2.9**



Scheme 2.3. Preparation of aryldithiols from sodium hydrogen sulfide.

2.4. Synthesis of cyclic(arylene disulfide) oligomers.

Iodine and DMSO are used most frequently to make disulfides or poly(disulfide)s from thiols.[38-40] Catalytic oxidation of dithiols by oxygen has seldom been used. Hay found that dithiols can be transformed into poly(disulfide)s by reaction with oxygen in the presence of a mixture of tertiary amine and a copper salt.[41] We have demonstrated that catalytic oxidation of aryldithiols is a very efficient and a novel way to synthesize cyclic(arylene disulfide) oligomers. The reactions are schematically illustrated in Scheme 2.4.



Scheme 2.4. Synthesis of cyclic(arylene disulfide) oligomers by a copper catalyzed oxidation reaction

The reaction products are mixtures of cyclic oligomers. Several solvents have been used for the synthesis. DMAc was found to be the best solvent for all the systems. The oxidation reaction is very fast and unlike other cyclization reactions, which are run over 16 h under high dilution condition[7-26], the present cyclization reactions are complete in 3 - 4 h with the formation of high yields of cyclic oligomers. The final concentration of the product based on the repeating unit is as high as 0.04 M, which is the same as that for typical nucleophilic process to make other cyclic oligomers.[22,23] It should be pointed out that vigorous stirring is very important for the reaction since oxygen has to be dispersed well into the reaction media. By this method, very high yields of cyclic oligomers were obtained (Table 2.1).

2.5. Characterizations of cyclic(arylene disulfide) oligomers.

2.5.1. Elemental analyses.

Elemental analyses (C, H, S) for all of the cyclic oligomers are shown in Table 2.1. Generally, sulfur contents are slightly lower than that of the calculated amount. We speculate that this maybe due to cyclic(arylene disulfide) oligomers which form

host-guest complexes with solvents[3] and the trapped solvents are extremely difficult to remove. The analysis results confirmed that cyclic(arylene disulfide) oligomers were formed by the catalytic oxidation.

Table 2.1. Elemental analyses of cyclic(arylene disulfide) oligomers.

Compoud	Yield(%)	Measured			Calculated		
		H	C	S	H	C	S
2.14a	85	3.32	58.85	37.88	3.25	58.03	38.72
2.14b	74	2.91	51.30	44.90	2.88	51.44	45.68
2.14c	95	3.63	66.12	30.73	3.73	66.63	29.64
2.14d	84	3.43	61.87	27.14	3.47	62.04	27.60
2.14e	98	5.37	68.30	22.80	5.46	69.72	24.81
2.14f	76	2.87	51.37	45.74	2.88	51.44	45.68
2.14g	93	-	33.97	30.17	-	33.99	30.24
2.14h	98	3.53	65.21	24.42	3.30	63.91	26.24
2.14i	85	3.53	67.80	19.17	3.47	68.94	18.40
2.14j	91	3.55	67.86	17.43	3.47	68.94	18.40
2.14k	88	4.07	76.34	12.34	4.03	76.77	12.81
2.14l	99	4.47	80.94	9.89	4.32	80.95	9.82
2.14m	76	3.07	60.87	22.99	2.96	61.74	23.54
2.14n	99	2.89	52.45	32.97	2.88	51.41	34.30
2.14o	85	4.15	62.42	18.19	3.82	63.50	18.84

* Elemental analyses (C, H, S) were performed by Fine Chemical Analysis in Ontario, Canada and Galbraith Laboratories, Inc. in Tennessee, USA. Methods used are based upon those found in "Standard Methods for the Examination of Water and Waste Water", 7th Ed., American Public Health Association, Washington.

2.5.2. Composition analyses of cyclic(arylene disulfide) oligomers.

Table 2.2. GPC analyses of cyclic(arylene disulfide) oligomers.

Cyclics	M_n(g/mol)	M_w(g/mol)
2.14a	560	720
2.14b	110	140
2.14c	700	760
2.14d	690	900
2.14e	1000	1700
2.14f	160	320
2.14g	370	390
2.14h	730	930
2.14i	880	1300
2.14j	640	700
2.14k	1400	2300
2.14l	1800	2800
2.14m	590	660
2.14n	470	490

The compositions of cyclic(arylene disulfide) oligomers were analyzed by GPC and gradient HPLC techniques. The GPC results are listed in Table 2.2 and some representive GPC charts are shown in Figure 2.1. These GPC results indicate that the products obtained by the present methods are low molecular weight oligomeric mixtures and their profiles are similar to that of typical cyclic oligomers.[7-26] Generally, ketone containing cyclic(disulfide) oligomers show higher apparent molecular weights since they are bulky molecules. Cyclic(disulfide) **2.14l** shows the

highest apparent molecule weight because of the presence of the very bulky tetraphenyl benzene moiety. Cyclic(disulfide) oligomers **2.14c** and **2.14j** are only slightly soluble in chloroform. Their GPC results represent only the soluble portion. It is unclear from these results whether they contain higher oligomers or linear polymers. Cyclic **2.14o** has a very strong interaction with the column and hence its GPC data is not available with chloroform as eluent.

The gradient HPLC charts for cyclic(arylene disulfide) oligomers **2.14a-n** (except **2.14j**) are shown in Figure 2.2. The gradient conditions were as follows: at 0 min, THF 70%, H_2O 30%; at 20 min, THF 90%, H_2O 10%; at 25 min , THF 100%; at 27 min, THF70%, H_2O 30%; at 30 min (end), THF 70%, H_2O 30%. Cyclic **2.14j** and **2.14o** are totally insoluble in THF, hence their gradient HPLC results are not available. The separation of cyclic oligomers by gradient HPLC is determined by the solubilities of and polarities of the substrates to be analyzed. Although we can generally apply the gradient conditions given above to analyze all of the cyclics obtained, cyclic oligomers **2.14n** were not well separated. The HPLC chart of **2.14n** was obtained by using the following gradient conditions: at 0 min, THF 60%, H_2O 40%; at 20 min, THF 80%, H_2O 20%; at 25 min , THF 100%; at 27 min, THF 60%, H_2O 40%; at 30 min (end), THF 60%, H_2O 40%.

From gradient HPLC and GPC results, we can assign repeating units for the cyclic(arylene disulfide) oligomers. The smallest repeating units of **2.14c** and **2.14f** are 3 (i.e. n=3), while that of **2.14g** is 4 (i.e. n=4). All other cyclic(arylene disulfide) oligomers **2.14** contain the smallest repeating unit , 2.

Scheme 2.5.

Oligomers **2.14a** contain 33% of cyclic dimer and 33% of cyclic trimer respectively, as determined by gradient HPLC, while **2.14d** contains 7.5% of cyclic dimer and 31% of cyclic trimer. This result may be because the distance between the two carbons is shorter in the aryl ether linkage than in the aryl thioether linkage (Scheme 2.5) and cyclics from the former would be more strained. Cyclic oligomers **2.14b** contain 47% of cyclic dimer due to the favorable conformation. All of the

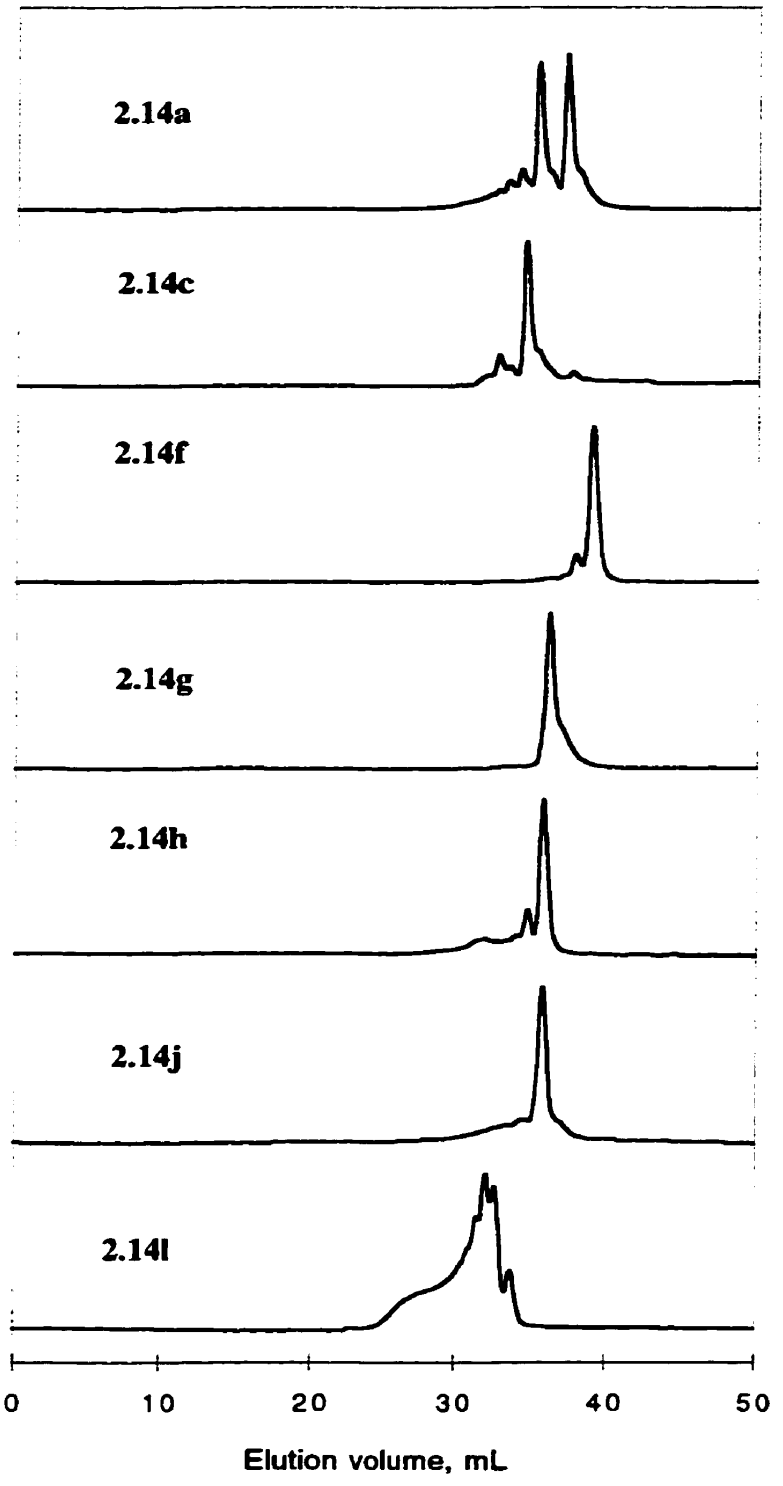


Figure 2.1 GPC charts of cyclic(arylene disulfide) oligomers

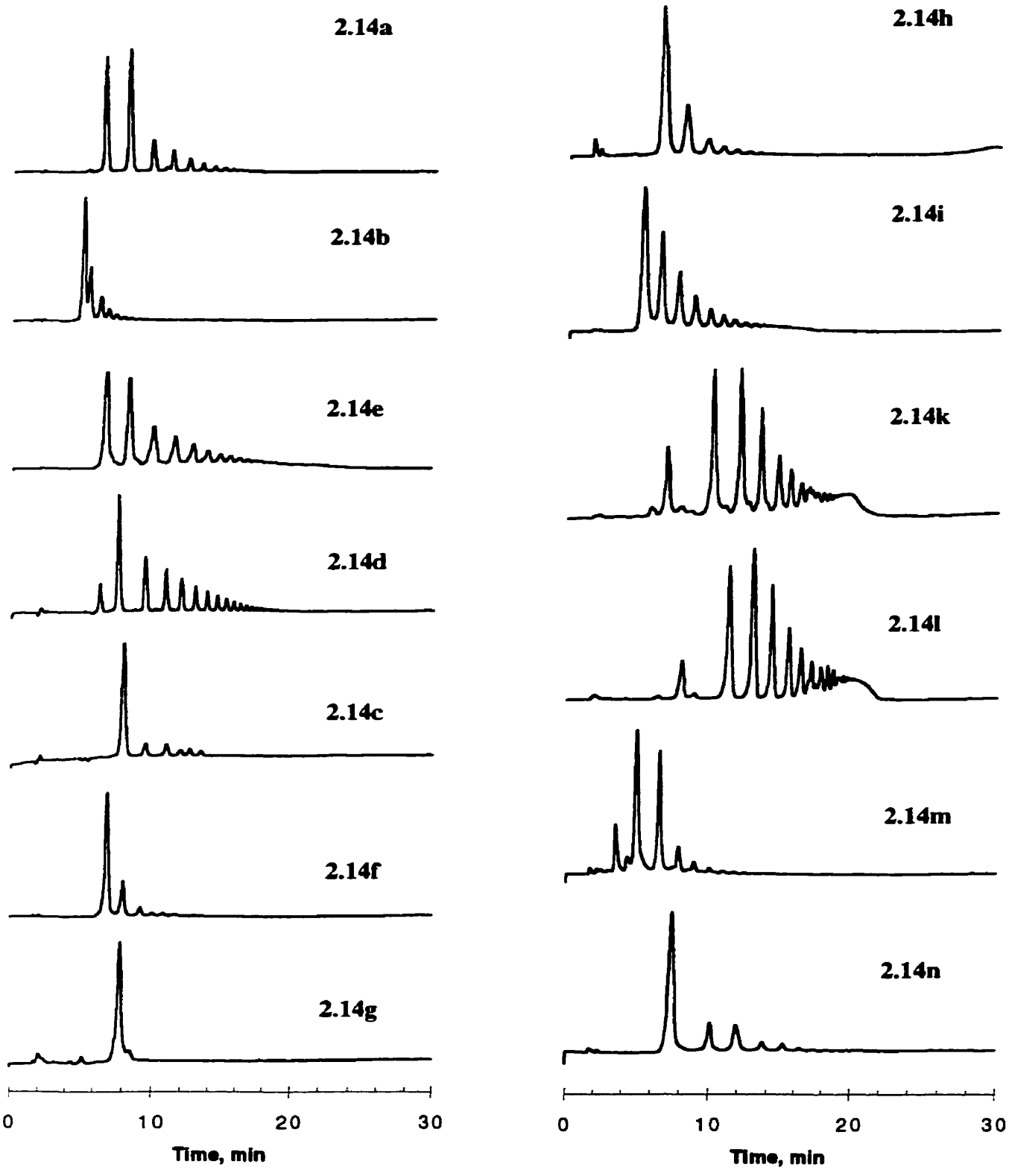


Figure 2.2 Gradient HPLC charts of cyclic(arylene disulfide) oligomers

cyclic oligomers **2.14e**, **2.14h**, **2.14i** and **2.14n** contain more cyclic dimer than cyclic trimer. Cyclic trimer and cyclic tetramer are dominant products for cyclic oligomers **2.14k**, **2.14l**, and **2.14m**. This is believed to be due to the ring strain in the cyclic dimers.

By gradient HPLC, **2.14f** contains 66% of trimer and 20% of tetramer, while **2.14g** contains 95% of tetramer. This distribution of the cyclic oligomers is consistent with the results obtained from other synthetic methods. By using iodine as oxidising agent and ethanol as solvent, the trimer of **2.14f** was obtained in 30% yield.[2] By the present method, cyclic oligomers **2.14f** were obtained in 76% yield and 66% of trimer was present. It is surprising to note that the tetramer of **2.14g** was the predominant product both in this method and in the DMSO method.[3] Apparently structural effects play an important role here. In particular, the fluorine atoms seem to exert some electrostatic repulsion which prevents the formation of a smaller cyclic oligomer (n=3) as in **2.14f**, with the analogous hydrogen-substituted ring.

2.5.3. Cyclic properties from NMR and MALDI-TOF-MS studies.

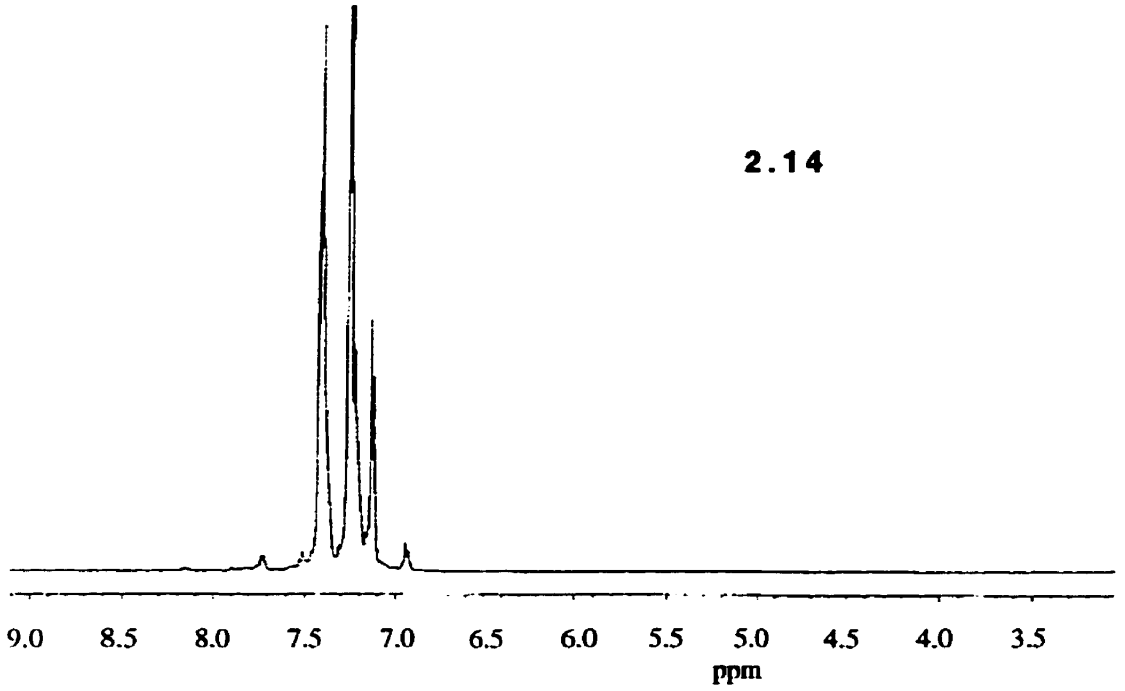


Figure 2.3. ^{1}H-NMR spectrum of **2.14a** in $CDCl_3$.

^{1}H-NMR spectra have been taken for all of the products to detect the presence of end groups. The ^{1}H-NMR spectrum of **2.14a**, shown in Figure 3, clearly shows that there is no proton signal due to a -SH group in the range of ppm 3-4. This indicates that there is no detectable -SH end group present in the products. The profiles of the HPLC and GPC chromatograms are consistent with those already reported for other oligomeric cyclic mixtures.[7-26] Therefore, we can reasonably state that the products obtained here are cyclic oligomers.

The cyclic structures have also been confirmed by MALDI studies. The MALDI-TOF-MS technique has been used recently to analyze linear polymers and has been particularly successful for oligomeric cyclic mixtures.[21,22,25,42-44] In the analysis of cyclic aromatic oligomers, no clean spectra were obtained without any matrix. By using 1,8,9-trihydroxyanthracene (dithranol) as matrix, a relatively clean spectra was obtained for **2.14o**. Repeating units up to 6 can be detected. However, no clean spectrum was obtained for other cyclic(arylene disulfide) oligomers under similar conditions. When silver was used as the cationization agent, no clean spectra were recorded. It was found that by adding LiBr as cationization agent, very clean MALDI spectra were obtained for **2.14i**, **2.14k** and **2.14l** (Figure 2.4). Cyclic oligomers **2.14j** with repeating units up to 3 are also detected by this technique, although the signal to noise ratio is lowThe repeating units up to 9 for **2.14k** (4523, M9+Li), **2.14l** (5890, M9+Li), and **2.14o** (3076, M9+Li), up to 10 for **2.14i** (3494, M10+Li) are clearly detected by this technique. The representive MALDI spetrum of **2.14k** is shown in Figure 4A. In the MALDI spectra for **2.14k**, **2.14i** and **2.14l**, small peaks corresponding to cyclic oligomers with one less sulfur atom were observed. The MALDI spectrum for cyclic oligomers **2.14o** consisted of two sets of molecular peaks (Figure 2.4B). One corresponds to cyclic oligomer peaks without the attachment of a Li cation. Another set corresponds to cyclic oligomers with the attachment of the Li cation. Without addition of any cationization agent, a relatively clean MALDI spetrum can be obtained. This indicates that cyclic oligomers **2.14o** can be easily charged for MALDI analysis. The addition of LiBr improved the analysis so that cyclic oligomers with repeating units up to 9, instead of 6 without the addition, were detected. Unfortunately, the MALDI-TOF-MS technique for other cyclic(arylene disulfide) oligomers failed to produce any spectra under various conditions tried.

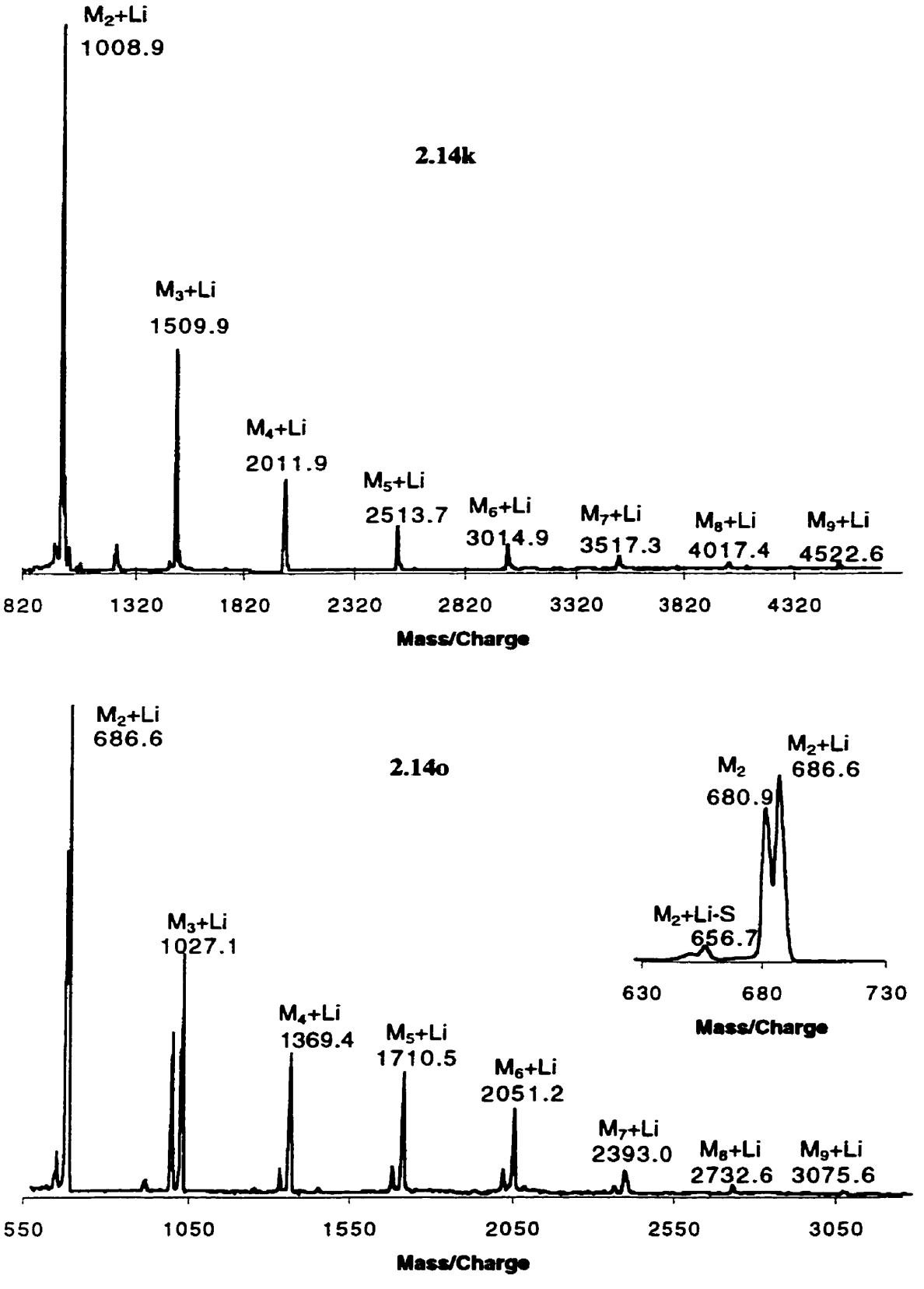


Figure 2.4 MALDI-TOF-MS spectra for cyclic(arylene disulfide) oligomers

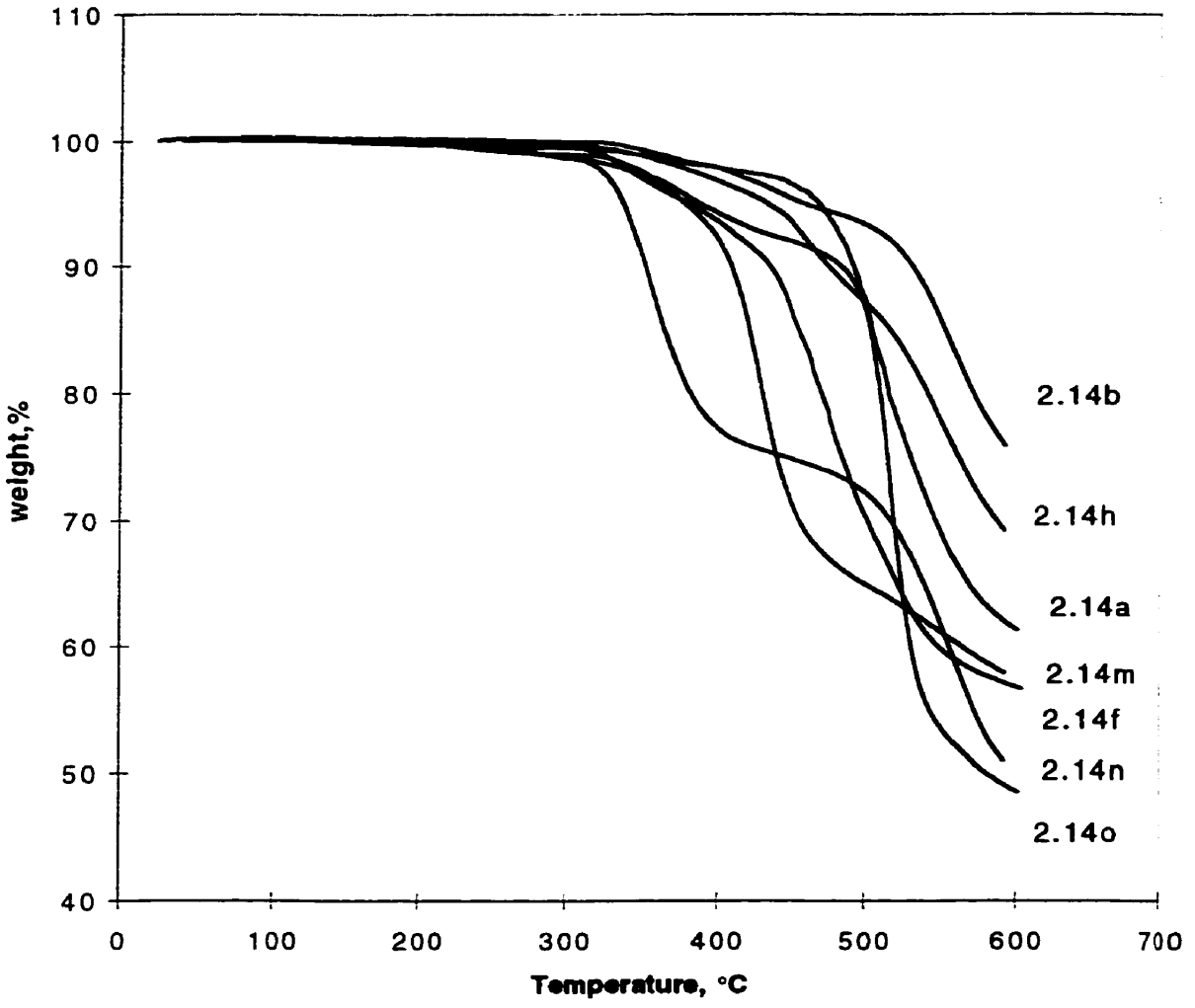


Figure 2.5 TGA scans of cyclic(arylene disulfide) oligomers

2.5.4. Thermoanalyses of cyclic(arylene disulfide) oligomers.

Table 2.3. Thermal properties of cyclic(arylene disulfide) oligomers.

Cyclics	DSC[a]				TGA[c] (-5%, N_2)
	1st scan			2nd scan	
	T_g (°C)	T_m (°C)	ΔH (kJ/mol)[b]	T_g (°C)	
2.14a	69.8	208.9	9.45	73	466
2.14b	-	155	9.14	38.1	376.3
2.14c	-	336.9	17.76	-	455.3
2.14d	76.9	-	-	78.7	407.1
2.14e	80.5	219.3	1.94	ND[d]	376.4
2.14f	-	220	7.01	74.3	380.2
2.14g	-	248.3	9.55	ND[c]	450.4
2.14h	-	226.3	9.7	149.7	433.6
2.14i	138.9	209.4	5.51	139	428.5
2.14j	-	318.3(dec.)	39.48	187.4	358.7
2.14k	189.9	-	-	190	441.2
2.14l	253.2	318.4.339.2	10.12	258	462.1
2.14m	-	260, 285	18.36	118.9	381.6
2.14n	-	303.4	16.88	214.5	336.9
2.14o	131.8	275.5	3.06	202.1	392.7

a. Measured under N_2, heating rate was 20 °C/min. b. Calculated based on repeating units. c. Temperature at which 5% weight loss was observed under N_2 atmosphere, heating rate was 20 °C/min. d. Not detected.

The cyclic(arylene disulfide) oligomers were tested using DSC and TGA, carried out at a heating rate of 20 °C/min under N_2 atmosphere (Table 2.3). All samples

were tested twice. The samples were first subjected to DSC heating as prepared. After the first heating scan, the sample was cooled down to room temperature and subjected to a second DSC analyses. Generally, the temperature limit for the first DSC heating scan was set at 320 °C. If no thermal features were detected below this temperature, the temperature limit was raised to 380 °C. For **2.14c** the limit was set at 400 °C to observe the thermal features and at this temperature significant weight loss occurred. Therefore, the second DSC heating scan for **2.14c** was not taken. All cyclic(arylene disulfide) oligomers, except **2.14d** and **2.14k**, show strong endothermic peaks in the first DSC heating scan which are due to melting; this may be due to the presence of significant amount of a cyclic dimer and trimer. Cyclic oligomers **2.14j** have the highest melting enthalpy. As expected, the biphenyl group increased the melting point significantly. Although the second DSC heating scans show that **2.14a** and **2.14d** have almost the same glass transition temperature, cyclic oligomers **2.14d** do not show any melting point or any crystallinity. Even though the second DSC heating scan suggested that cyclic(arylene disulfide) oligomers containing ketone, sulfone, and phosphine oxide groups have higher glass transition temperatures than their ether or thio-ether counterparts, they only show a slight increase in their melting points (Table 2.3). Therefore, the melt ring-opening polymerization of cyclic(arylene disulfide) oligomers are very feasible and practical since melt ring-opening polymerization of cyclic oligomers have to be carried out above the melting points. The T_gs of cyclic oligomers from the second heating scan show the same correlation with structure effects as other polymer systems. The T_g of sulfone containing cyclic oligomers **2.14n** are 50 °C higher that that of ketone containing **2.14h**. The tetraphenyl benzene moiety containing cyclic oligomers **2.14l** have the highest T_g among those studied.

The 5% weight loss temperatures from TGA analyses for these cyclic(arylene disulfide) oligomers are above 350 °C, and even up to 450 °C; an exception was **2.14n** which showed 5% weight loss at 337 °C. Weight loss generally starts from ca. 320 °C (Figure 2.5). At high temperatures, there is an equilibrium reaction existing for diphenyl disulfide.[45] Diphenyl disulfide produces diphenyl sulfide and sulfur by a thermolysis reaction and diphenyl disulfide can also be formed by reaction of diphenyl sulfide and sulfur. This equilibrium reaction explains the thermal stability characteristics of cyclic(arylene disulfide)s. This is also the reason why cyclic(arylene disulfide) oligomers lose weight starting around 320 °C. **2.14n** has the least thermal stability which is due to loss of sulfur dioxide. Oae *et al.* have shown that the reaction of diphenylsulfone and diphenyl disulfide produces sulfur dioxide at 300 °C.[46] It can

be seen that the initial weight loss of cyclic oligomers **2.14n** are roughly equal to the weight loss of sulfur dioxide.

2.6. Conclusions

A series of cyclic(arylene disulfide) oligomers have been synthesized by a copper catalyzed oxidation reaction with oxygen and characterized by several techniques. The cyclic(arylene disulfide) oligomers generally have solubilities in common organic solvents, such as DMAc and chloroform. Repeating units up to 10 have been detected by the MALDI-TOF-MS technique for some cyclic(disulfide) oligomers. Almost all of the cyclic(arylene disulfide) oligomers show sharp melting points by DSC which indicates they are semi-crystalline. TGA analysis of cyclic(arylene disulfide) oligomers indicates that 5% weight losses are above 350 °C and some up to 450 °C.

2.7. Experimental Section

Gradient HPLCs were performed on a Milton Roy CM4000 multiple solvent delivery system with a C8 Prime Sphere 4.6x250 mm column, THF and water as eluent solvents, and a UV detector at 300 nm. GPC analyses were performed on a Waters 510 HPLC equipped with 5μ phenogel columns (linear, 3x500 Å) arranged in series with chloroform as solvent and a UV detector at 254 nm. DSC scans were obtained using a Seiko 220 DSC instrument at a heating rate of 20 °C/min in N_2 (160 mL/min). The weight loss data were obtained from a Seiko 220 TG/TGA instrument at a heating rate of 20 °C/min in nitrogen. NMR data were recorded at 500 MHz on a Varian UNITY500 NMR instrument and are listed in parts per million downfield from tetramethylsilane. Elemental analyses (C, H, S) were performed by Fine Chemical Analysis in Ontario, Canada and Galbraith Laboratories, Inc. in Tennessee, USA. Matrix assisted laser desorption ionization - time of flight - mass spectroscopy (MALDI-TOF-MS) analyses were performed on a Kratos KOMPACT-MALDI-TOF-MS. The analyte consisted of 1.0 : 4.0: 200 (w) of cyclic oligomers, lithium bromide and 1,8,9-trihydroxyanthracene (Dithranol) matrix. A sample (0.2 μL) of this analyte was spotted on the sample slot and air-dried. Melting points were taken on a Fisher-Johns melting point apparatus and the thermometer was uncorrected.

All the chemicals used were reagent grade and purified by standard methods. The required 4,4'-thiobis(benzenethiol) (**2.9a**) and 1,3-benzenedithol (**2.9b**) were purchased from Aldrich Chemical Inc. Other aryldithiols were prepared according to

the methods illustrated in Schemes 2-4. N,N'-Dimethyl thiocarbamoylchloride (Aldrich), chlorosulfonic acid (Omega) and sodium hydrogen sulfide monohydrate (Fluka) were used as received.

Starting materials **2.13j**, **2.13k**, and **2.13l** were prepared according to literature procedures.[47] **2.13i** was synthesized according to the published procedure.[48] **2.13o** was prepared by a Grignard technique[49]. Other starting materials were purchased from chemical suppliers.

4,4'-Biphenyldithiol (**2.9c**) and 4,4'-oxybis(benzenethiol) (**2.9d**) were prepared according to reported procedures.[50] 4,4'-Bis(1-mercaptophenylene)-2,2'-propane (**2.9e**) was prepared by the route illustrated in Scheme 1. 1,4-Benzenedithiol (**2.9f**) and terafluoro-1,4-benzenedithiol (**2.9g**) were synthesized by the methods given in the literature.[3,51]

Bis(4-chlorosulfonylphenyl)2,2'-propane (2.8e).

A 250 mL round-bottom flask was charged with 65 mL of chlorosulfonic acid and cooled to *ca.* - 10 °C. 2,2'-Diphenyl propane (25.0g, 0.127 mol) was added to the reaction mixture over 2 h via a dropping funnel. The resulting mixture was warmed to room temperature and kept at this temperature for 4 h. Then, it was poured carefully into 1 kg of ice. The product was extracted with ca. 300 mL of toluene and the organic solvent was evaporated to dryness with a rotary evaporator. The resulting solid was recrystallized from acetic acid and dried at room temperature under vacuum. Yield: 25.6 g, 50.7%. m. p. 154-156 °C. ^{1}H NMR ($CDCl_3$): δ7.98 (d, 4H, J = 7.81 Hz), 7.46 (d, 4H, J = 7.81Hz), 1.79 (s, 6H, CH_3). ^{13}C NMR ($CDCl_3$): δ156.9, 142.4, 128.1, 127.2, 44.3, 30.1.

Bis(4-mercaptophenyl)2,2'-propane (2.9e).

Compound **2.8e** (25.0 g, 0.063mol) prepared above was added to a 1000 mL of round-bottom flask charged with 300 mL of absolute ethanol, 300 mL of concentrated hydrochloric acid and 250 g of stannous chloride dihydrate. The resulting mixture was heated to reflux for 8 h. After cooling, it was diluted with 1000 mL water and filtered. The solid was dissolved in 5% NaOH solution and precipitated out by adding diluted HCl. This procedure was repeated three times and then the material was recrystallized from ethanol. Yield: 11.2 g, 77.6%. m. p. 66-67 °C (lit.[21] 69-70 °C). ^{1}H

NMR ($CDCl_3$): δ7.17 (d, 4H, J = 8.1 Hz), 7.07 (d, 4H, J = 8.1 Hz), 3.38 (s, 2H, SH). ^{13}C NMR ($CDCl_3$): δ148.1, 129.4, 127.6, 127.5, 42.3, 30.5.

4,4'-Dimercaptobenzophenone (2.9h).

Sodium hydrogen sulfide monohydrate 22.2 g was dissolved in DMF (100 mL) by heating to reflux. After cooling, 4,4'-difluorobenzophenone (10.91 g, 0.05 mol) was added carefully to the flask and the reaction mixture was kept at reflux for 5 h (**caution: H_2S, which must be trapped and oxidized by passing through a 30% NaOH solution and a bleach solution, is produced during the reaction!**). The reaction mixture was then allowed to cool to room temperature and the precipitated salt was filtered. The filtrate was diluted with 200 mL water and acidified with a 5% HCl solution. The precipitate was collected by filtration, then dissolved in 5% NaOH solution and reprecipitated by adding 5% HCl solution. This purification process was repeated three times and the solid product was dried at room temperature under vacuum. Yield: 9.20 g (74.7%). m. p. 171-174 °C (lit.[36] 178, ethanol). ^{1}H-NMR ($CDCl_3$): δ7.65 (d, 4H, J = 6.4 Hz), 7.33 (d, 4H, J = 6.4 Hz), 3.64 (s, 2H, SH).

The following compounds were similarly prepared but using the reagents described in Scheme 2.4. In all cases, the amounts of difluoro or dichloro compounds used were 0.05 mol.

1,3-Bis(4-mercaptobenzoyl)benzene (2.9i).

Yield: 91.0%. m.p. 178-181 °C. ^{1}H-NMR ($CDCl_3$): δ8.10 (s, 1H), 7.97(m,2H),7.70 (d, 4H, J = 8.3 Hz), 7.62(m, 1H), 7.34(d, 4H, J = 8.3 Hz), 3.67 (s, 2H, SH). HRMS: Found: 350.0433 (64.8%); Calcd for $C_{20}H_{14}O_2S_2$: 350.0435.

1,2-Bis(4-mercaptobenzoyl)benzene (2.9j).

Yield: 91.4%. m.p. 156-158 °C (toluene) . ^{1}H-NMR ($CDCl_3$): δ7.59 (s, 4H), 7.56 (d, 4H, J = 8.3 Hz), 7.22 (d, 4H, J = 8.3 Hz), 3.62 (s, 2H, SH). HRMS: Found: 350.0433 (64.8%); Calcd for $C_{20}H_{14}O_2S_2$: 350.0435.

1,2-Bis(4-mercaptobenzoyl)-3,6-diphenylbenzene (2.9k).

Yield: 89.2%. m.p. 165-168 °C (toluene). ^{1}H-NMR ($CDCl_3$): δ7.59 (s, 2H), 7.40 (d, 4H, J = 7.8 Hz), 7.21(m, 10H), 6.99(d, 4H, J = 7.8 Hz), 3.46 (s, 2H, SH). HRMS: Found: 502.1065 (100%); Calcd for $C_{32}H_{22}O_2S_2$: 502.1061.

1,2-Bis(4-mercaptobenzoyl)-3,4,5,6-tetraphenylbenzene (2.9l).

Yield: 93.2%. m.p. 203-204 °C (toluene). ^{1}H-NMR ($CDCl_3$): δ7.43 (d, 4H, J = 7.8 Hz), 7.00(d, 4H, J = 7.8 Hz), 6.85(m, 20H), 3.46 (s, 2H, SH). HRMS: Found: 654.1685 (100%); Calcd for $C_{44}H_{30}O_2S_2$: 654.1687.

4,4'-Mercaptobenzil (2.9m).

Yield: 96.2%. m.p. 140-141 °C. ^{1}H-NMR ($CDCl_3$): δ7.81 (d, 4H, J = 8.3 Hz), 7.33 (d, 4H, J = 8.3 Hz), 3.71 (s, 2H, SH). HRMS: Found: 274.0124 (4.5%); Calcd for $C_{14}H_{10}O_2S_2$: 274.0122.

Bis(4-mercaptophenyl)sulfone (2.9n).

Yield: 61.0%. m.p. 137-139 °C (toluene). ^{1}H-NMR ($CDCl_3$): δ7.44 (d, 4H, J = 8.3 Hz), 7.32 (d, 4H, J = 8.3 Hz), 3.65 (s, 2H, SH). HRMS: Found: 281.9844 (100%); Calcd for $C_{12}H_{10}O_2S_3$: 281.9843.

Bis(4-mercaptophenyl)phenylphosphine oxide (2.9o).

Yield: 81.6% m.p.74-76 °C. ^{1}H-NMR ($CDCl_3$): δ7.63 (t, 2H, J = 7.8 Hz,PhH), 7.55 (d, 2H, J = 6.8 Hz, PhH), 7.50(s, 1H, PhH), 7.47(d, 4H, J = 10.3 Hz), 7.32(d, 4H, J = 10.3 Hz), 3.63(s, 2H, SH). HRMS: Found: 342.0298 (100%); Calcd for $C_{18}H_{15}OPS_2$: 342.0302.

General procedure for preparation of cyclic(arylene disulfide) oligomers.

A 500 mL three neck round bottom flask equipped with a condenser, a dropping funnel and oxygen inlet was charged with 0.5g CuCl, 1.1g N,N,N',N'-tetramethylethylene diamine (TMEDA) and 200 mL DMAc. The mixture was vigourously stirred for 15 min with oxygen bubbling directly into the reaction mixture. Then, 0.1 mol of the aryldithiol dissolved in 50-100 mL of DMAc was added dropwise to the reaction mixture over 2 h. The resulting mixture was stirred for another hour to

ensure the completion of the reaction and was then filtered through a layer of alumina. The filtrate was treated with 300 mL of 5% HCl solution and further stirred for 1 h. The precipitate was collected by filtration and dried at 50 °C under vacuum for 48 h.

For the preparation of **2.14c**, **2.14h**, and **2.14j**, the products are not soluble in DMAc, and the resulting reaction mixtures were poured into 500 mL of 5% HCl solution directly without filtration and stirred for 3 h to remove the copper salt. This procedure was repeated three times.

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Chapter 3. Ring-opening Polymerization of Cyclic(arylene disulfide) Oligomers

3.1. Introduction

Poly(aliphatic disulfide)s have long been commerciallized and have found many applications. The Thiokol company in the U.S.A marketed the first synthetic polysulfide rubber in 1929 and it remains the main producer today. Cured poly(disulfide)s have high resistance to enviromental degradation, good low-temperature properties, low water-vapor transmission, good adhesion to wood, metal, glass and concrete and have excellent resistance to solvents, water, acids and bases. Due to their importance in industry and academia, there are several reviews devoted to this class of polymers.[1-4] Contrary to the extensive studies of poly(aliphatic disulfide)s, little information is available about poly(arylene disulfide)s, which can be mainly attributed to their insolubility. Ghafoor *et al.* synthesized a polyquinazolone containing a disulfide group which showed increased ductility and decreased hardness upon curing due to the presence of the flexible disulfide linkage.[5] Bis(4-hydroxyphenyl)sulfone treated with S_2Cl_2 forms an hydroxy functionalized polyaryldisulfide.[6] Several poly(arylene disulfide)s, including polybiphenyldisulfide, have been synthesized from difunctional sulphenyl chlorides and dithiols. NMR and molecular weight data are not available for these materials because they are not soluble in common solvents.[7] DMSO was used as the oxidizing agent to prepare poly(*m*-phenylene disulfide) from dithioresorcinol. The number average molecular weight of the polymer obtained was 880 (DP *ca.* 6) and intrinsic viscosity in NMP at 30 °C was 0.11 dL/g. The oligomers were further chemically modified by chlorosulfonic acid and showed a conductivity of $1x\ 10^{-5}$ S cm^{-1}.[8] Using oxidative coupling with oxygen catalyzed by copper salts and an amine, Hay was able to prepare a series of polyarylene disulfides which were not soluble in common organic solvents, and which were not fully characterized.[9]

Recent research has been carried out to prepare high performance polymers from cyclic oligomers to solve processing problems such as low solvent solubility and high melt viscosities.[10-15] Although it is routine to prepare poly(aliphatic disulfide)s

by ring-opening polymerization of cyclic(aliphatic disulfide)s,[16] little attention has been given to the ring-opening polymerization study of cyclic(arylene disulfide)s.[17]

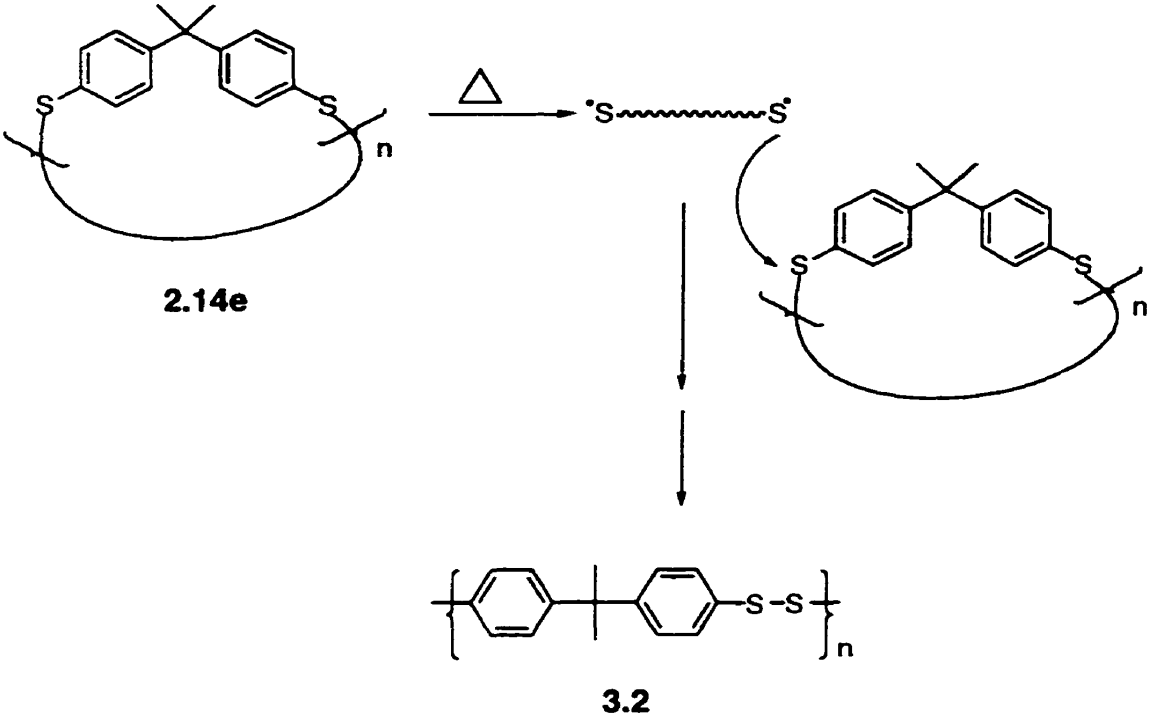
3.2. Strategy and goals

In the previous chapter, we have described the synthesis of a series of cyclic(arylene disulfide) oligomers, which were obtained in high yields and have high solubilities. The solubility of cyclic(arylene disulfide) oligomers provides a means for the purification, which is unlikely for high molecular weight poly(arylene disulfide)s due to their highly insolubility. Combined with the low melt viscosity of cyclic oligomers, the melt ring-opening polymerization of cyclic oligomers should be a very promising method to manufacture poly(arylene disulfide)s. However, the high insolubity of poly(arylene disulfide)s is still a big obstacle to fully study and understand the ring-opening polymerization reactions. Cyclic(arylene disulfide) oligomers with medium melting points, which provide soluble poly(arylene disulfide)s, are highly desirable to study the aforementioned technique. Fortunately, by examing all the cyclic(arylene disulfide) oligomers synthesized in the previous chapter, we found that cyclic oligomers **2.14e** derived from 4,4'-isopropylidene bis(benzenethiol) (**3.1**) meet all the requirements. The cyclic oligomers have a T_g of 81 °C and a melting point 219 °C (range 195-223 °C), which provide a poly(arylene disulfide) readily soluble in common organic solvents such as chloroform and tetrahydrofuran. Herein we describe in detail the study of the ring-opening polymerization reaction for the cyclic(disulfide) oligomers **2.14e**. This study provides understanding of the ring-opening polymerization reactions of cyclic(arylene disulfide) oligomers.

3.3. Ring-opening polymerization of cyclic(arylene disulfide) oligomers 2.14e in solution

The ring-opening polymerization was first conducted in diphenyl ether solution without adding any catalyst and monitored by GPC. There are numerous reports of ring-opening polymerization of cyclic(aliphatic disulfide)s catalyzed by base or acids[3]. However, there are only a few reports of ring-opening polymerization of cyclic(disulfide)s without any catalyst. In 1972, Hiatt found some cyclic bis(arylene tetrasulfide)s undergo instant ring-opening polymerization upon heating.[18] A 1,2,3-trithiane was reported to form a high molecular weight polymer upon standing in a closed flask at room temperature over 12 h.[19] We found that cyclic(disulfide)s underwent ring-opening polymerization in the absence of a catalyst. It is well known

that the disulfide bond ruptures to form radicals at elevated temperatures.[20] This property has been utilized to prepare poly(*p*-phenylene sulfide) and to initiate ring-opening polymerization of cyclic oligomers containing thioether linkages.[13,21] Therefore, one can conclude that **2.14e** forms radical species upon heating which initiate the ring-opening polymerization reaction (Scheme 3.1).



2.14e **3.2**

Scheme 3.1. Ring-opening polymerization of cyclic(arylene disulfide) oligomers

The GPC traces of products from the ring-opening polymerizations of **2.14e** at 150 °C for different times are shown in Figure 3.1. For comparision, the GPC trace of cyclic oligomers **2.14e** are shown in Figure 3.2. Figure 3.1 indicates that the ring-opening polymerization was very slow at this temperature. The conversion to polymers increased at longer reaction times. High molecular weight polymers formed in spite of the low conversion, which is a characteristic of a typical chain growth free radical polymerization reaction. When the polymerization temperature was raised to 200 °C, high molecular weight poly(disulfide) formed almost instantly with less than 20% of cyclic remaining. Examining Table 3.1, we can see that the molecular weights of poly(arylene disulfide)s from the ring-opening polymerization reaction are independent of reaction time, however, they depend on the reaction temperatures.

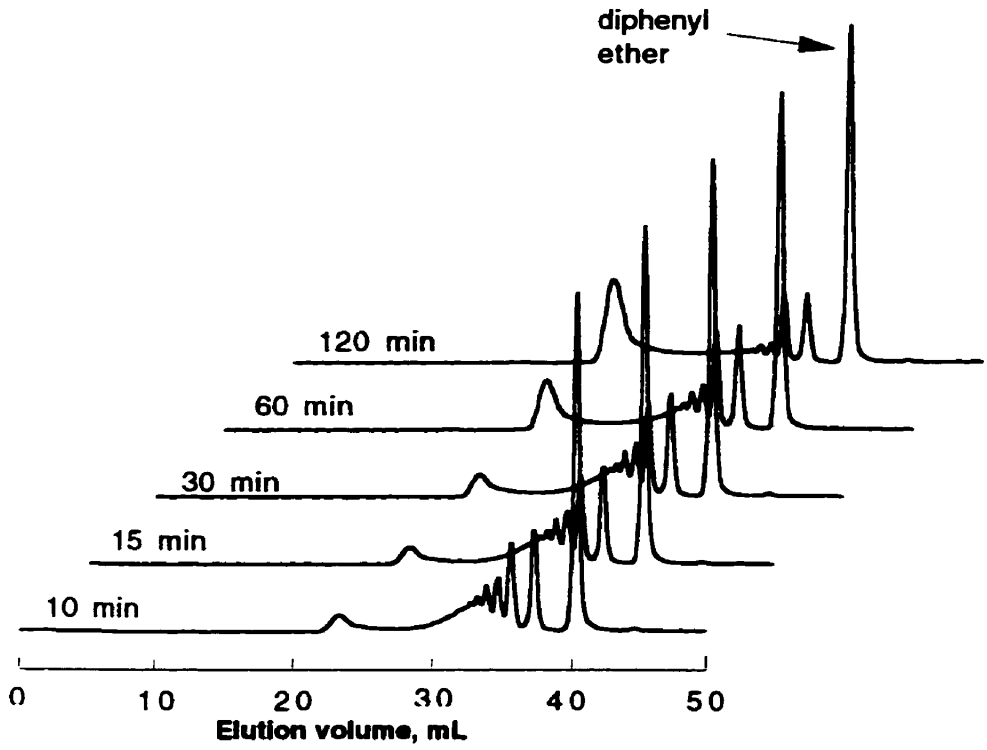


Figure 3.1. GPC charts for ring-opening polymerization of **2.14e** at 150 °C in diphenyl ether solution.

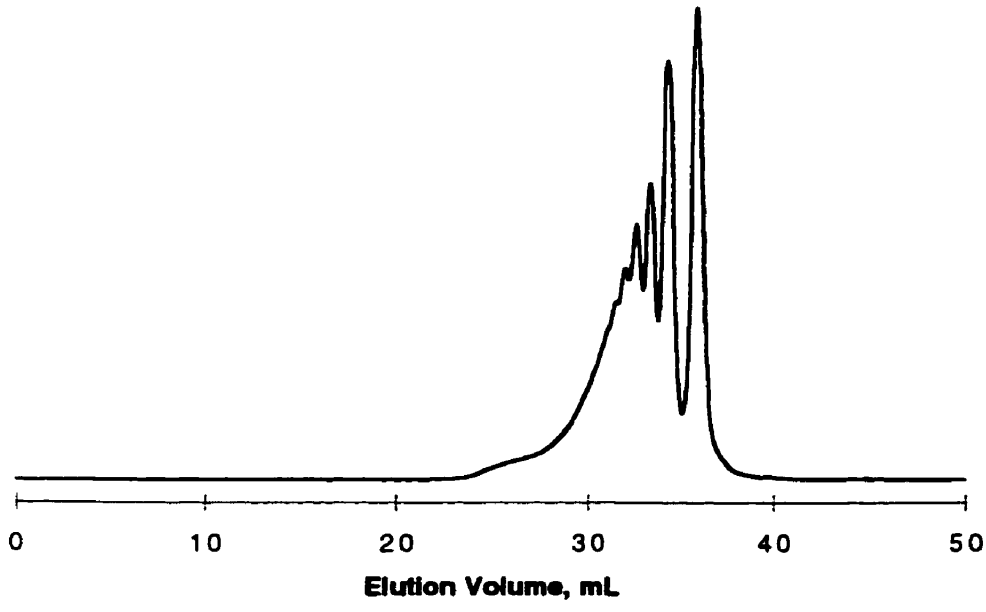


Figure 3.2. GPC trace of cyclic(arylene disulfide) oligomers **2.14e**.

Under the examined conditions, the highest molecular weight polymers were formed at 200 °C. Above this temperature, the higher the temperature, the lower the molecular weights of polymers formed by ring-opening polymerization. For example, the weight average molecular weight of polymer **3.2** formed at 200 °C in a 15 min reaction was 108,000. However, the molecular weights were 62,000 and 52,000, respectively, at 250 °C and 300 °C under the same conditions (Table 3.1). A cross-linking reaction with the formation of insoluble products occured above 300 °C.

Table 3.1. GPC results of ring-opening polymerization in diphenyl ether solution.

Temperature(° C)	Time (min)	M_n(g/mol)	M_w(g/mol)	Conversion of cyclics(%)
150	10	47,000	80,000	6
	15	43,000	75,000	7
	30	41,000	70,000	12
	60	49,000	90,000	24
	120	53,000	106,000	60
200	10	64,000	123,000	82
	120	62,000	125,000	83
250	10	27,000	51,000	98
	120	26,000	60,000	97
300	10	27,000	54,000	98
	120	25,000	64,000	98*

* Soluble portion.

3.4. Ring-opening polymerization of cyclic(arylene disulfide) oligomers 2.14e in the melt

Encouraged by the results from solution ring-opening polymerization, we carried out the ring-opening polymerization in the melt. Soluble poly(disulfide)s were obtained below 300 °C. No polymerization was observed at 150 °C, even for 2 h, as detected by GPC. Ring-opening polymerization took place almost instantly around 200 °C (Table 3.2). The typical cyclic oligomers start to melt around 195 °C as detected by

DSC. The results indicate that ring-opening polymerization of cyclic oligomers does not take place below the melting point. However, the movements of cyclic molecules are assisted by solvents, hence in solution the ring-opening polymerizations can take place well below the melting points.

Table 3.2. GPC results of ring-opening polymerization in the melt.

Temperature (°C)	Time (min)	M_n(g/mol)	M_w(g/mol)	Cyclics remaining (%)
150	15	1000	1700	100
	120	1000	1700	100
200	15	88,000	189,000	1.6
	120	88,000	211,000	1.4
250	15	30,000	97,000	1.5
	30	30,000	111,000	1.6
	120	39,000	282,000	1.5
300	15	4,400	14,500	soluble portion
	30	1,900	10,000	soluble portion
	120	1,200	4,300	soluble portion

High molecular weight polymers were formed for melt ring-opening polymerization at 200 °C with only trace amounts of cyclic oligomers remaining. Again, we found that molecular weights of the polymers formed from ring-opening polymerization reaction are independent of the reaction time, however they depend on the reaction temperatures. The highest molecular weight polymers were obtained by reaction at 200 °C. Increase of the reaction temperature resulted in the decrease of the molecular weights of polymers. Presumably, this is due to the decomposition of disulfide bonds in the polymer chain at higher temperatures. Branching also occurred at higher temperatures and at much longer reaction times, which resulted in polymers with high polydispersities at 250 °C. At the same reaction temperatures, the molecular weights were higher for polymers obtained in the melt than for polymers obtained from solution, which could be due to ring-chain equilibration in solution.

A cross-linking reaction occured at temperatures above 300 °C and insoluble black products were obtained in all cases. Below 300 °C, soluble poly(arylene disulfide) **3.2** can be obtained. There is no reaction between the thiyl radical and methyl group even for two hours reaction below 250 °C. Below 300 °C the thiyl radical reacts with disulfide group first to form polymers. In previous studies, we also found that the thiyl radical *ipso*-substitutes iodine to form an aromatic sulfide by reacting with *p*-iodotoluene at 280 °C.[22,23]

The thermal properties of a typical polymer were measured by differential scanning calorimetry and thermogravimetric analysis at a heating rate of 20 °C/min under an atmosphere of nitrogen. This polymer was obtained by ring-opening polymerization at 200 °C for 15 min. It had a T_g of 126 °C. The 5% weight loss temperature of this polymer was 369 °C.

3.5. Structure of the poly(arylene disulfide) 3.2

To study the structures of the poly(disulfide)s from ring-opening polymerization, an authentic poly(disulfide) polymer was prepared by oxidative polymerization of the corresponding dithiol compound.[9] A white fibrous high molecular weight polymer was obtained after a 2 h polymerization reaction. The polymer is readily soluble in common organic solvents. The apparent number average molecular weight was 90,000 and weight average molecular weight was 131,000 as determined by GPC using polystyrenes as standards. The polymer is virtually identical to the polymers obtained at 200 °C from ring-opening polymerization.

^{1}H-NMR spectra for dithiol compound **3.1**, cyclic oligomers, poly(disulfide) **3.2** from ring-opening polymerization at 200 °C for 15 min and **3.2**, from direct oxidation reaction were taken in $CDCl_3$ solution and are shown in Figure 3.3. Aromatic proton signals became much more complex because of the formation of cyclics (Figure 3.3B). However, the signals after the ring-opening polymerization became simpler (Figure3.3C) and were the same as that of authentic poly(disulfide) (Figure 3.3D). The proton signals of H_1 for cyclic oligomers and poly(disulfide)s are downfield compared to dithiol compound **3.1**, because the disulfide group is at a higher oxidation state than the thiol group.

^{13}C-NMR spectra of cyclic(disulfide) oligomers, poly(disulfide) **3.2** from ring-opening polymerization at 200 °C for 15 min and that from direct oxidation are shown in Figure 3.4. Again, we observed the complex carbon signals of cyclic oligomers became simpler after ring-opening polymerization reaction. Poly(disulfide) from ring-

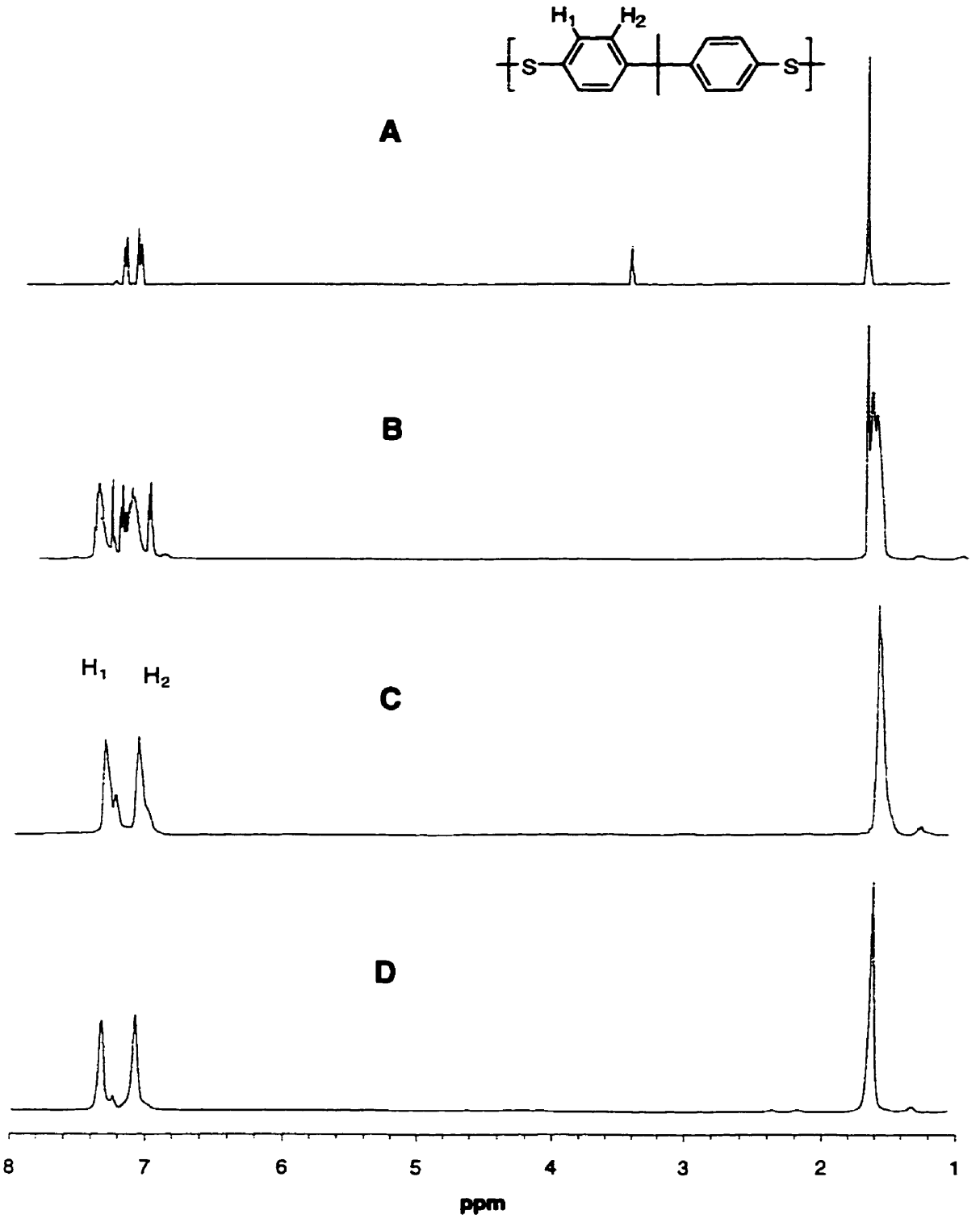


Figure 3.3. ^{1}H-NMR spectra. (A). **3.1**; (B). cyclic(disulfide) oligomers **2.14e**; (C). poly(arylene disulfide) **3.2** from melt ring-opening polymerization at 200 °C for 15 min. (D). poly(arylene disulfide) **3.2** from direct oxidative polymerization.

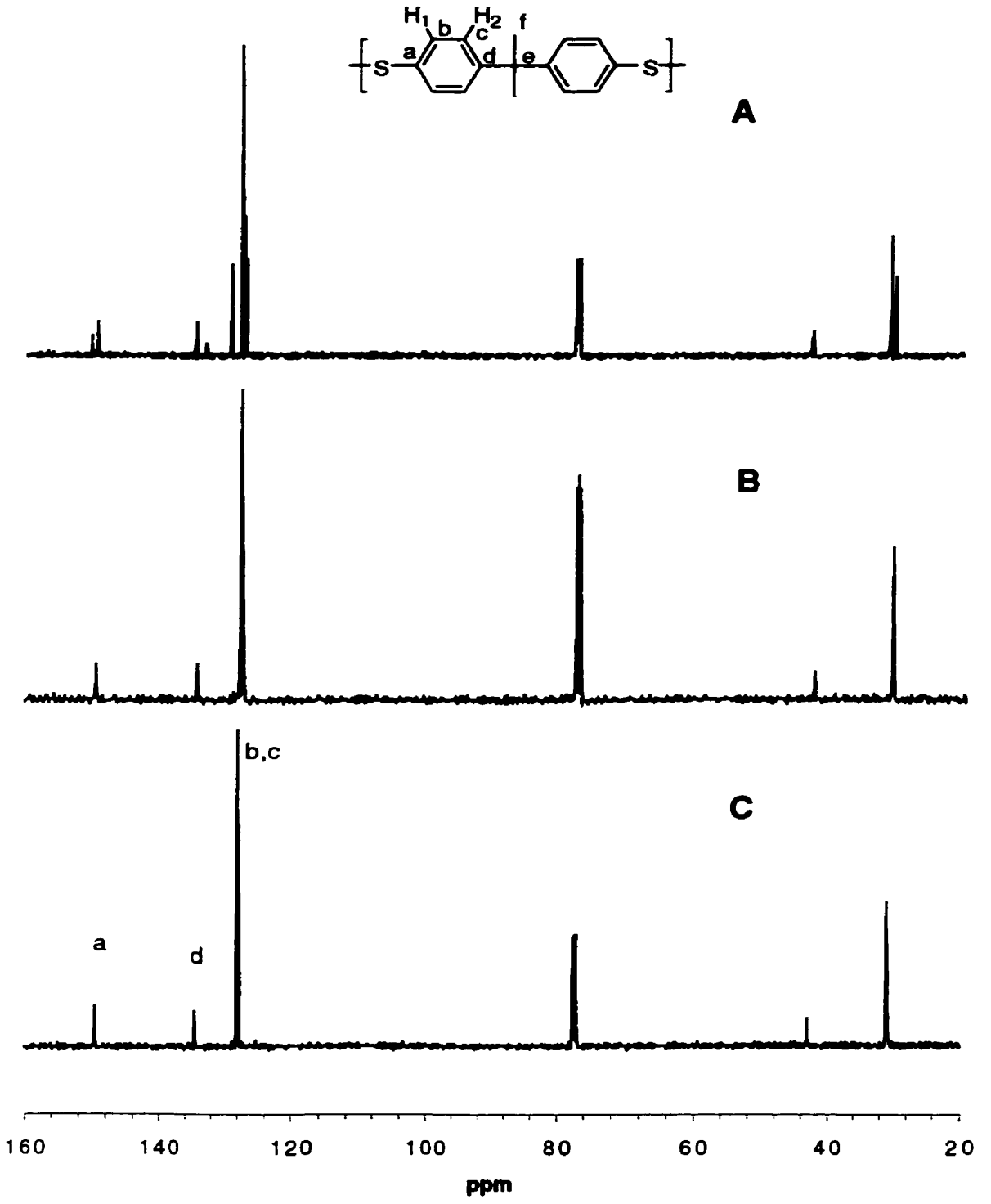


Figure 3.4. ^{13}C-NMR spectra. (A). cyclic(disulfide) oligomers **2.14e**; (B). poly(arylene disulfide) **3.2** from melt ring-opening polymerization at 200 °C for 15 min. (C). poly(arylene disulfide) **3.2** from direct oxidative polymerization.

opening polymerization showed exactly the same ^{13}C signals as that of authentic poly(disulfide). Therefore, we can conclude that poly(disulfide) **3.2** obtained by ring-opening polymerization at 200 °C is a structurally regular poly(disulfide).

However, the structural regularity decreased as the ring-opening polymerization temperature increases as evidenced by ^{13}C-NMR spectra. Several extra peaks appeared for **3.2** when the polymerization was carried out at 250 °C, presumably because of the formation of trisulfide bonds and/or thioether bonds. It is well documented that thermolysis of diphenyl disulfide at high temperatures (*ca.* 250 °C) produces diphenyl sulfide and elemental sulfur.[24] Diphenyl disulfide or diphenyl trisulfide can also be formed by reaction of diphenyl sulfide or diphenyl disulfide with sulfur. The higher the reaction temperature, the more complex the polymer structures.

3.6. Ring-opening polymerization of other cyclic(arylene disulfide) oligomers

Table 3.3. Thermal properties of poly(arylene disulfide)s from ring-opening polymerization of cyclic(arylene disulfide) oligomers*

Cyclic oligomers	T_g (°C)
2.14a	73
2.14b	37
2.14d	79
2.14e	116
2.14f	70
2.14h	149
2.14i	138

* Ring-opening polymerizations were conducted at 250 °C for 30 min. T_gs were obtained from DSC testing at heating rate of 20 °C/min under nitrogen atmosphere.

Melt ring-opening polymerizations for other cyclic(arylene disulfide) oligomers have also been briefly studied. Based on the results obtained from ring-opening

polymerization of cyclic(disulfide) oligomers **2.14e**, the melt ring-opening polymerizations were conducted at 250 °C for 30 min to ensure that structurally regular poly(arylene disulfide)s were obtained. As expected, only thermal transitions corresponding to the glass transitions were observed for those cyclic(disulfide) oligomers with melting points below 250 °C, indicating the formation of polymers. For those cylic disulfide oligomers with melting point higher than 250 °C (**2.14c**, **2.14l**, *etc.*), no ring-opening reactions were detected since the glass transition temperatures are still the same as those for cyclic(disulfide) oligomers. GPC studies indicated that the cyclics were intact after heating at 250 °C for 30 min. The T_gs of the poly(arylene disulfide)s obtained from melt ring-opening polymerization are listed in Table 3.3. The T_g for the polymer obtained from **2.14a** is 73 °C, which is around 12 °C lower than that of PPS. This is attributed to the more flexible linkage of -S-S- compared with -S-.

Poly(arylene disulfide) **3.3** from cyclic(arylene disulfide) oligomers **2.14a** forms a flexible film and a TMA analysis was carried out on this film (Figure 3.5). At 25 °C, it has a Young's modulus of 1.02 E+09 Pa. Tan δ of this polymer is 83 °C.

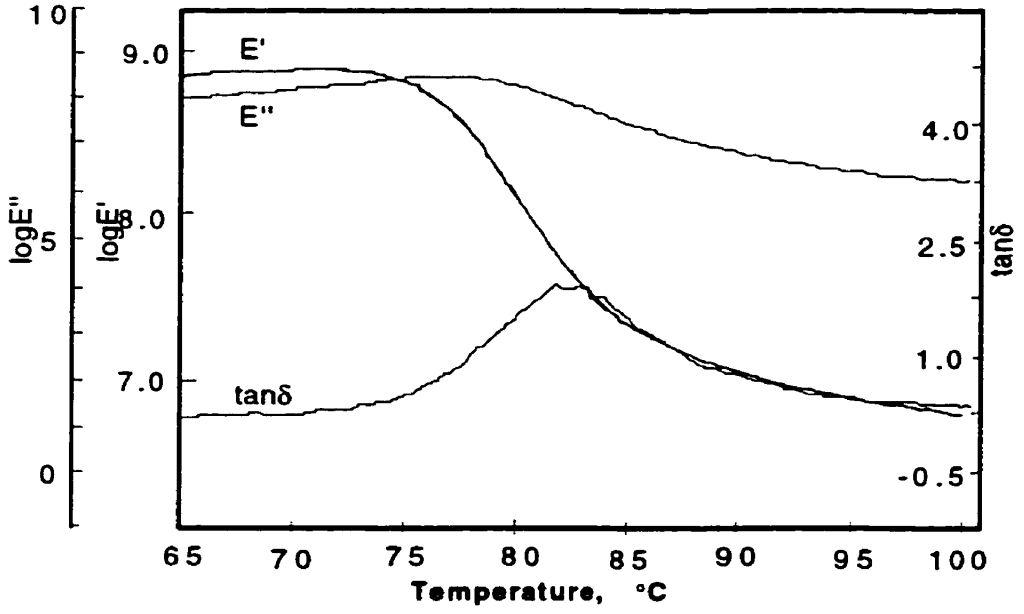


Figure 3.5. TMA charts of poly(arylene disulfide) **3.3** from melt ring-opening polymerization of **2.14a**

3.7. Conclusions

The ring-opening polymerization reaction of the oligomeric cyclic(disulfide) **2.14e** was conducted both in diphenyl ether solution and in the melt. The reaction took place at 150 °C in solution, however, it only took place at 200 °C or above in the melt. The ring-opening polymerization reaction was very rapid above *ca.* 150 °C. The highest molecular weight polymers were formed at 200 °C. Structurally regular poly(disulfide)s were obtained below 250 °C, however, structural irregularities were introduced above 250 °C. The ring-opening polymerizations were also briefly studied for other cyclic(arylene disulfide) oligomers, which form high molecular weight poly(arylene disulfide)s with excellent solvent resistance.

3.8. Experimental section

Materials

Cyclic(arylene disulfide) oligomers **2.14e** were synthesized from 4,4'-isopropylidene bis(benzenethiol) as described in chapter 2. The cyclic oligomers contain 26% of dimer, 22% of trimer, 14% of tetramer, 11% of pentamer, and other higher oligomers as measured by gradient HPLC. ^{1}H NMR spectra indicated that the cyclic oligomers do not contain any detectable -SH end groups. The GPC trace of this cyclic oligomers is shown in Figure 3.2. Differential scanning calorimetry (DSC) of the cyclic mixtures shows a T_g of 81 °C and a melting point 219 °C (range 195-223 °C). Reagent grade diphenyl ether and DMAc were purchased from Aldrich. Cuprous chloride was purchased from J. T. Baker, and N,N,N',N'-tetramethylethylenediamine was purchased from Lancaster.

Analytical procedure

GPC analyses were performed on a Waters 510 HPLC equipped with 5μ phenogel columns (linear, 3x500 Å) arranged in series with chloroform as solvent and a UV detector at 254 nm. The apparent molecular weight data were reported with polystyrenes as standards. DSC scans were obtained using a Seiko 220 DSC instrument at a heating rate of 20 °C/min in N_2 (160 mL/min). The weight loss data were obtained from a Seiko 220 TG/TGA instrument at a heating rate of 20 °C/min in nitrogen. TMA analyses were carried on a Seiko TMA / SS 120 instrument. ^{1}H-NMR data (TMS reference) and ^{13}C-NMR data (solvent reference) were recorded at 500 MHz and 125 MHz respectively on a Varians UNITY500 NMR machine with $CDCl_3$ as solvent.

General procedure for ring-opening polymerization in solution

A Pyrex test tube (1.5 x 15 cm) equipped with a nitrogen inlet and a mini magnetic stirring bar was charged with 200 mg of cyclics and 1 mL of diphenyl ether and immersed in a preheated salt bath to a depth of about 2 cm to cover the contents. From time to time, aliquots for GPC analysis were taken with a pipette and quenched with chloroform.

General procedure for ring-opening polymerization in the melt

The cyclic sample (~ 10 mg) was placed on a DSC aluminum pan and was heated under nitrogen atmosphere with a flow rate of 200 mL/min on a Seiko 220 TGA/DTA instrument. After cooling, the resulting material was subjected to either NMR or GPC analysis.

The ring-opening polymerization was also carried out on 200 mg of cyclic samples in test tubes under nitrogen atmosphere.

Synthesis of poly(arylene disulfide) 3.2 by direct oxidation

A 25 mL of three-neck round bottom flask equipped with a oxygen inlet, a condenser, a thermometer and a magnetic stirrer was charged with 5 mL of DMAc, 0.20g (2.0 mmol) of CuCl, and 0.38 g (3.3 mmol) of N,N,N'N'-tetramethylethylenediamine (TMEDA). The reaction mixture was vigorously stirred for 5 min while oxygen was bubbled in. Then, 1.0 g (3.8 mmol) of 4,4'-isopropylidene bisthiophenol in 2 mL of DMAc was added in one portion. After stirring for another 2 h, the reaction mixture was poured into 100 mL of diluted HCl solution to precipitate out polymer. The solid was filtered and redissolved in 20 mL of chloroform. The chloroform solution was filtered through a thin layer of alumina, concentrated, and coagulated in methanol. The fibrous polymer was recovered by filtration and dried under vacuum at 100 °C for 24 h.

Ring-opening polymerization of cyclic(disulfide) oligomers 2.14a

The cyclic oligomers (150 mg) were placed on a piece of aluminium foil and the foil was folded into a 2 x 1 cm rectangle. The rectangle was placed on the surface of a hot plate which was preset at 260 °C for 30 min, during which the rectangle was pressed with a piece of glass. After cooling down, the aluminium foil was removed and the resulting brown film was subjected to analysis.

3.9. References and notes

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Chapter 4. Copolymerization of Elemental Sulfur with Cyclic(arylene disulfide) Oligomers

4.1. Introduction

It is well documented that elemental sulfur undergoes thermal polymerization at elevated temperatures and converts back to the cyclic octamer below 160 °C (floor temperature).[1,2] Anionic copolymerization of elemental sulfur with cyclic aliphatic mono- or polysulfides has resulted in stable high molecular weight polymers with sulfur contents ranging from 1 to 9 sulfur linkages.[3,4] Prior to this work, no successful copolymerization between elemental sulfur and cyclic(sulfide)s had been reported. The polycondensation of dihaloalkanes with alkali metal polysulfides is a well known reaction for the preparation of both linear and network polysulfide polymers.[1] The resulting polysulfanes have good weatherability and aging properties and are inert to organic solvents. Although there have been extensive studies on poly(aliphatic sulfane)s, reports on poly(arylene sulfane)s are limited. Bis(arylene tetrasulfide)s undergo spontaneous ring-opening polymerization to give poly(arylene sulfane)s at elevated temperatures.[5] 1,4-Dichlorobenzene reacts with elemental sulfur and forms high molecular weight linear poly(1,4-phenylene sulfane) in the presence of metallic lithium at room temperature. The sulfur content in this polymer reaches up to three S atoms per phenylene unit.[6]

4.1. Strategy and goals

In the chapter 2, we have synthesized a series of cyclic(arylene disulfide) oligomers prepared by oxidative coupling of aromatic dithiols with oxygen using a copper-amine catalyst. The cyclic(arylene disulfide) oligomers undergo melt ring-opening polymerization and form high molecular weight linear poly(arylene disulfide)s, which were described in chapter 3. We envisioned that the copolymerization between cyclic(arylene disulfide) oligomers should give stable high molecular weight linear poly(arylene sulfane)s with high sulfur contents. Fortunately, cyclic(arylene disulfide) oligomers **2.14e** provided soluble poly(arylene sulfane)s with different sulfur contents, which enabled us to study the copolymerization reactions in detail. Based on studies on cyclic(disulfide) oligomers **2.14e**, we further studied the copolymerization

reactions between cyclic(disulfide) oligomers **2.14a** and element sulfur, which provide stable rubbery poly(arylene sulfane)s with excellent solvent resistances.

4.3. Solution copolymerization of cyclic(disulfide) oligomers 2.14e with elemental sulfur

Since ring-opening polymerization of cyclic(disulfide) oligomers give soluble high molecular weight polymers, it is conceivable that polysulfanes obtained from copolymerization of these cyclic(disulfide) oligomers with elemental sulfur should be soluble, at least for lower sulfur content polymers. Experiments were first carried out in solution to evaluate the potential for the free radical copolymerization between cyclic(disulfide) oligomers **2.14e** and elemental sulfur. The reactions were followed with GPC by taking aliquots from time to time. Under the GPC conditions used, the presence of free sulfur can be detected at a retention time of around 47 minutes. Therefore, the free sulfur contents in the reaction mixture were determined with GPC by using diphenyl ether as a quantative calibration reference. A typical GPC chart from the attempted solution copolymerization reaction is shown in Fig. 4.1. The chart shows the formation of high molecular weight polymer as well as the presence of free sulfur. High molecular weight polymers formed immediately when the mixtures were heated above 150 °C. Regardless of the reaction temperatures, there was always about 15% of cyclic oligomers remaining, as determined by GPC. This phenomenon was also observed for solution ring-opening polymerization of cyclic(disulfide) oligomers **2.14e**, which is presumably caused by the ring-chain equilibration in the solution. The changing of molecular weights of copolymers formed as temperature changes is similar to that in the ring-opening polymerization reaction. Regardless of the amounts of S_8 added to the reaction mixtures, the molecular weights of copolymers from solution copolymerizations are almost the same for the same reaction temperatures. At 150 °C, copolymers with M_n = 45,000, M_w = 73,000 were formed, while copolymers with M_n = 50,000, M_w = 108,000 were formed at 200 °C. When the reaction took place at 250 °C, lower molecular weight polymers with M_n = 30,000, M_w = 60,000 were formed. From GPC analyses, polymers with sulfur contents ranging from 3-4 S groups per polymer unit were formed. Copolymers with higher sulfur contents cannot be formed regardless the amount of S_8 added. When the higher amounts of S_8 were added, more free sulfur was detected at the end of the reaction. When the amount of sulfur added was enough to theoretically produce 8 sulfur linkages in the polymer chain, there was about 75% free sulfur left at the end of reaction, even after a reaction

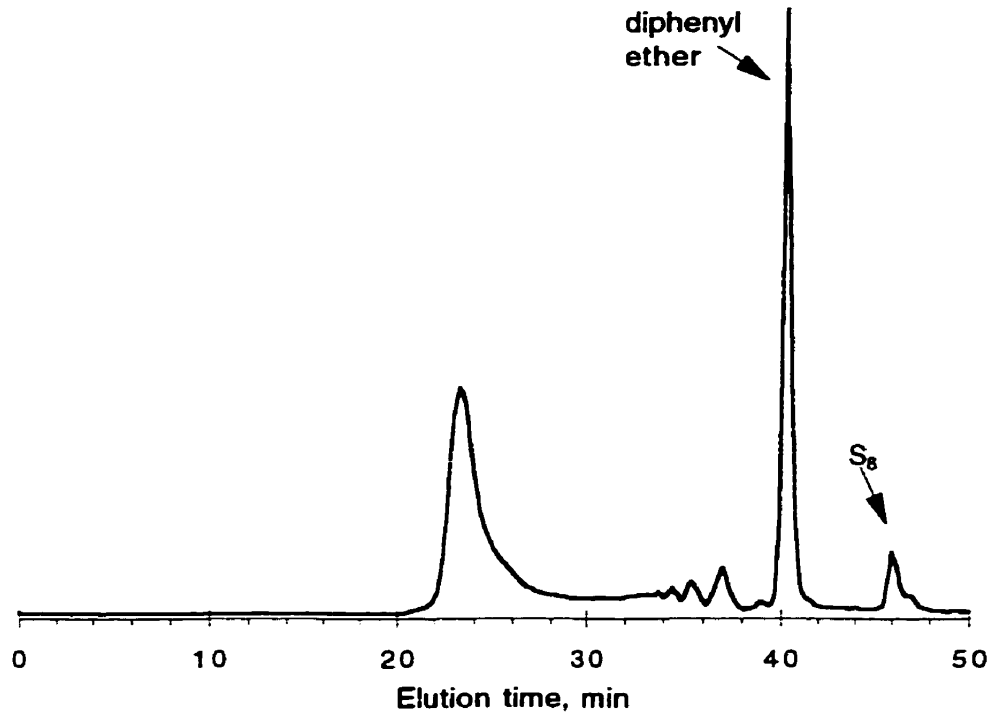


Figure 4.1. Typical GPC chart for solution copolymerization between cyclic(disulfide) oligomers **2.14e** and elemental sulfur.

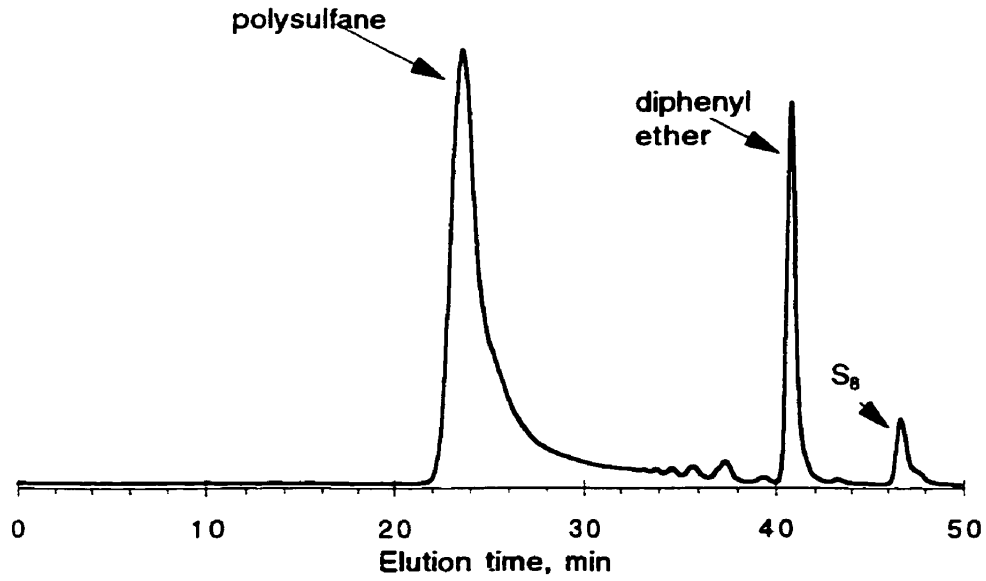
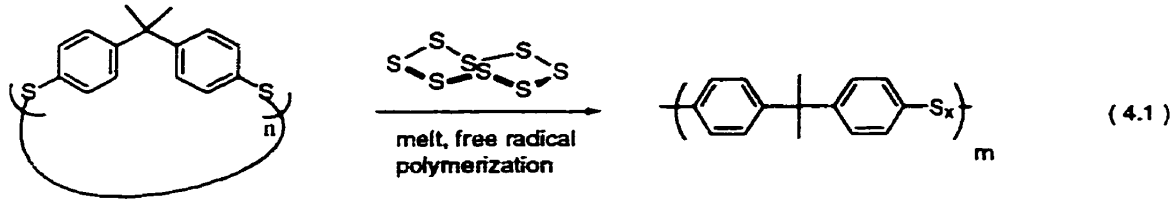


Figure 4.2. Typical GPC chart for melt copolymerization between cyclic(disulfide) oligomers **2.14e** and S_8. (Diphenyl ether was added to quantitively determine the amount of free sulfur. This result is for a 1 h melt copolymerization reaction betweent 1 equivalent of cyclic(disulfide) oligomers and 4 equivalents of sulfur at 200 °C .)

time of 24 h. Presumably, the difficulty of forming copolymers with high sulfur contents is due to the ring chain equilibration with S_8.

4.4. Melt copolymerization of cyclic(disulfide) oligomers 2.14e with elemental sulfur



(4.1)

2.14e **4.1**

In contrast to the copolymerization in solution, copolymerization of cyclic(disulfide) oligomers **2.14e** with S_8 in the melt gave polymers with much higher sulfur contents. Experiments were carried out for copolymerizations of 1 equivalent of cyclic(disulfide) oligomers **2.14e** (based on the repeating unit) with 1, 2, 3, 4, 5, and 6 equivalents of sulfur. Based on the studies of solution copolymerization and ring-opening polymerization of cyclic(disulfide) oligomers **2.14e**, we chose to study in detail the melt copolymerization at 150 °C and 200 °C. Higher temperatures would be expected to give polymers with lower molecular weights and more complex structures.

With the addition of 1 equivalent of sulfur, at 150 °C, the copolymerization reaction proceeded similiar to that of ring-opening polymerization reaction of the cyclic oligomers themselves. High molecular weight polymers (M_n = 40,000, M_w = 80,000) formed immediately with most of the cyclic oligomers remaining. When more sulfur was added, the melt copolymerization at 150 °C was much faster than that of ring-opening polymerization of cyclic(disulfide) oligomers **2.14e** at the same temperature. High molecular weight polymers formed immediately with much less of the cyclic oligomers remaining. When 2 equivalents of sulfur were added, polymers with M_n = 53,000, M_w = 89,000 were formed after 15 minutes with around 75% of cyclic oligomers remaining. After 30 minutes, around 24% of cyclic oligomers remained. Only about 15% of cyclic oligomers were left after 1 hour reaction and only a trace amount of free sulfur was detectable, which indicates the formation of polytetrasulfides (average). The melting point of the cyclic oligomers **2.14e** is 219 °C (range 195-223 °C). The addition of free sulfur makes the melting points much lower, hence facilitates

the melt copolymerization reaction at 150 °C. With the addition of 3, 4, 5 and 6 equivalents of sulfur, high molecular weights polysulfanes formed in 15 minutes with only trace amount of cyclic oligomers remaining. The resulting polysulfanes are very soluble in $CHCl_3$ when 4 equivalents or less of sulfur were added. However, the polysulfanes become less soluble with the addition of 5 or more equivalents of sulfur. In these cases, the molecular weights obtained by GPC only represent the soluble parts of the resulting materials.

Table 4.1. GPC results of melt copolymerization of cyclic(disulfide) oligomers **2.14e** and S_8. (reaction time: 2 h)

Temperature (°C)	x[a]	M_n[b]	M_w[b]	Free sulfur (%)	Conversion of cyclics (%)
150	3	84,000	156,000	0	28
	4	70,000	119,000	0	85
	5	81,000	142,000	2	95
	6	78,000	138,000	15	98
	7	56,000[c]	98,000[c]	23	99
	8	69,000[c]	119,000[c]	27	98
200	3	84,000	163,000	0	96
	4	70,000	153,000	0	97
	5	65,000	138,000	1	99
	6	77,000	161,000	2	99
	7	67,000[c]	140,000[c]	10	-
	8	79,000[c]	146,000[c]	20	-

a. Calculated number of sulfurs linked in the polysulfanes.

b. GPC, the eluent was $CHCl_3$ and the calibration standards were polystyrenes..

c. Soluble portion.

The copolymerization reaction took place much faster at 200 ℃ and gave polysulfanes with almost the same molecular weights as those obtained at 150 ℃ (Table 4.1). Even when one equivalent of sulfur was added, a high molecular weight polytrisulfide formed in 15 minutes with only a trace amount of cyclic oligomers and free sulfur remaining.

The free sulfur contents in the final products were determined by GPC analyses. A typical GPC chart is shown in Figure 4.2, which clearly shows the formation of high molecular weight polysulfanes with unreacted free sulfur remaining. Although the formation of high molecular weight polymers took place very rapidly, the incorporation of free sulfur in the polymer chain is slower. The free sulfur amounts in the reaction mixture decreased as the reaction time increased. With the addition of 6 equivalents of sulfur, at 200 °C, about 80 % of the sulfur added was copolymerized with the cyclic(disulfide) oligomers after 2 hours reaction time and the amount did not increase any further at longer times. This indicates that polysulfanes with maximum (average) of 6-7 sulfur linkages can be formed in 2 hours via the copolymerization between cyclic(disulfide) oligomers and elemental sulfur. Amounts of elemental sulfur in excess of that will remain intact. With less sulfur added, the copolymerization reaction is completed within 2 hours. When only 1 equivalent of sulfur was added, only a trace amount of free sulfur was detectable after 15 minutes when reaction took place at 200 °C. The reaction between 5 equivalents of sulfur and 1 equivalent of cyclic(disulfide) oligomers **2.14e** at 200 ℃ also gave polysulfanes with 6-7 sulfur linkages, since only 10% of free sulfur was detected after 2 hours reaction.

^{1}H-NMR spectra were taken for the products obtained after 2 hours of reaction. A singlet peak for the methyl group at δ = 1.6 ppm is present for all the products. Two singlet peaks (δ = 7.35 ppm, and 7.10 ppm) were observed for the arylenetrisulfide moiety. Two groups of multiple peaks were observed for other polyarylene sulfides groups (δ = 7.44 ppm and 7.13 ppm). The ^{13}C-NMR spectra, shown in Figure 4.3, give further structural information. In comparision with the ^{13}C-NMR spectrum of the poly(disulfide) from melt ring-opening polymerization, the ^{13}C-NMR spectra for polysulfanes with different number of sulfur linkages show a group of new peaks at around 131 ppm due to the downshift of one of the carbon signals, and all other existing peaks became much more complicated at the same time. The spectra shown in Figure 4.3 for polysulfanes containing $x \geq 6$ represent only the soluble portion of the polymers; most of the those polymers are insoluble in $CHCl_3$.

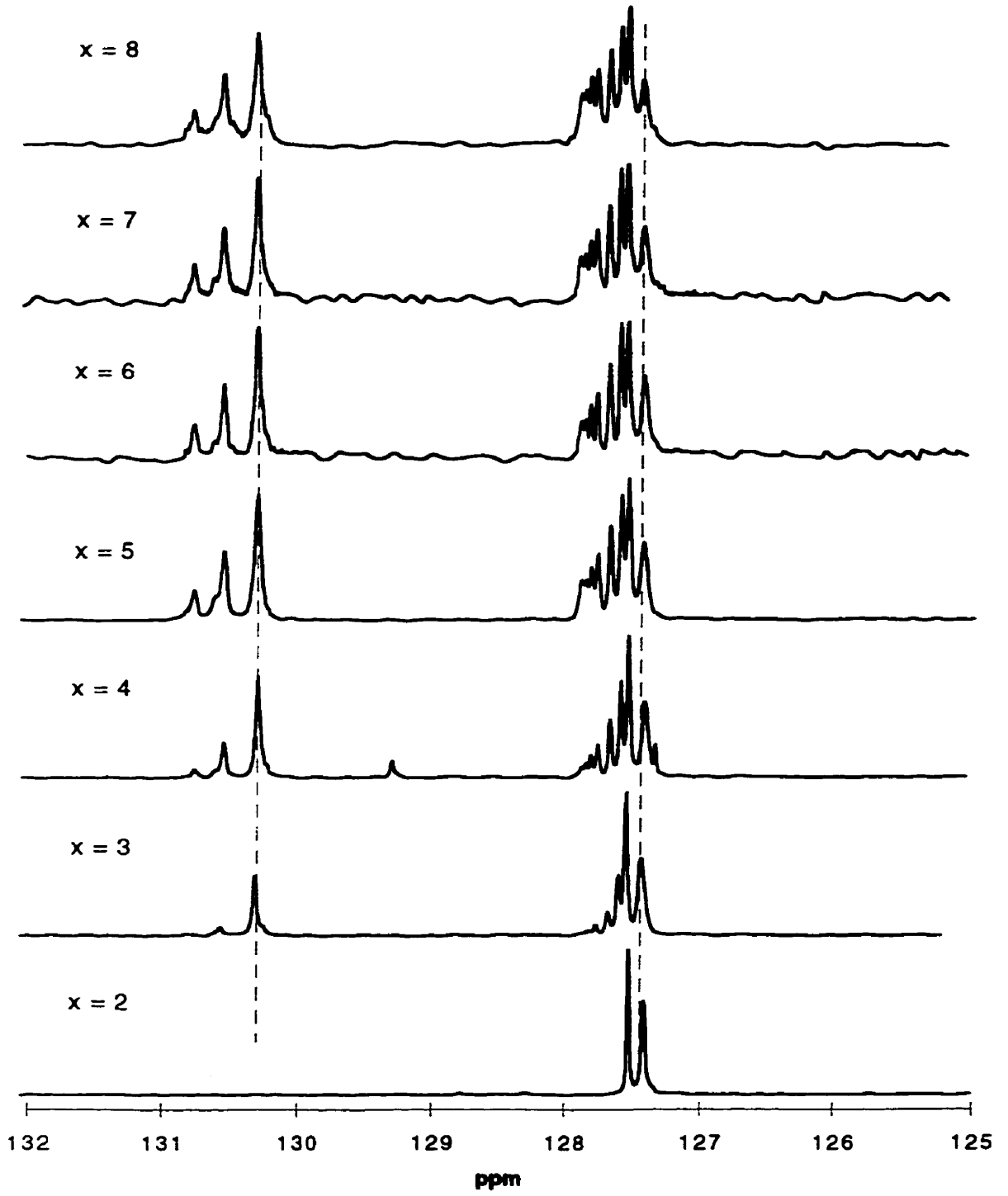
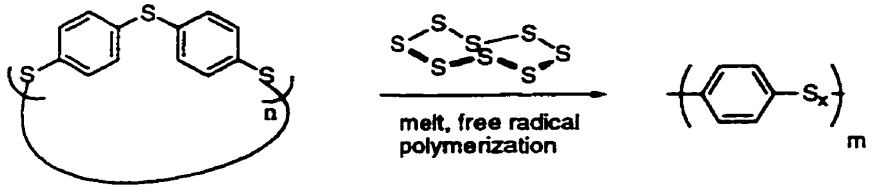


Figure 4.3. ^{13}C-NMR spectra of polysulfanes **3.1** obtained from melt copolymerization reactions.

4.5. Melt copolymerization of cyclic(disulfide) oligomers 2.14a with elemental sulfur

Melt copolymerizations of elemental sulfur with cyclic(disulfide) oligomers **2.14a** were also conducted. Since the resulting polysulfanes are insoluble in common organic solvents at room temperature, no molecular weight information was obtained. One different feature of these cyclic oligomers is that they contain a thioether linkage, which is also reactive with sulfur and can form mutiple sulfur linkages.[7] Therefore, the resulting polymers are poly(phenylene sulfane)s (Equ. 4.2).



n = 2, 3, 4, ...

2.14a **4.2** (4.2)

Table 4.2. Properties of polysulfanes **4.2** obtained from melt copolymerization reactions. (reaction time: 2 h)

No.	Sulfur linkage (x)	Tg (°C)	TGA[b] (°C)	Tan δ (°C)
1	2[a]	84	459	108
2	3	50	342	73
3	4	38	303	59
4	5	22	280	53
5	6	21	285	52
6	7	12	249	44

a. Poly(disulfide) from melt ring-opening polymerization reaction.

b. 5% weight loss temperature.

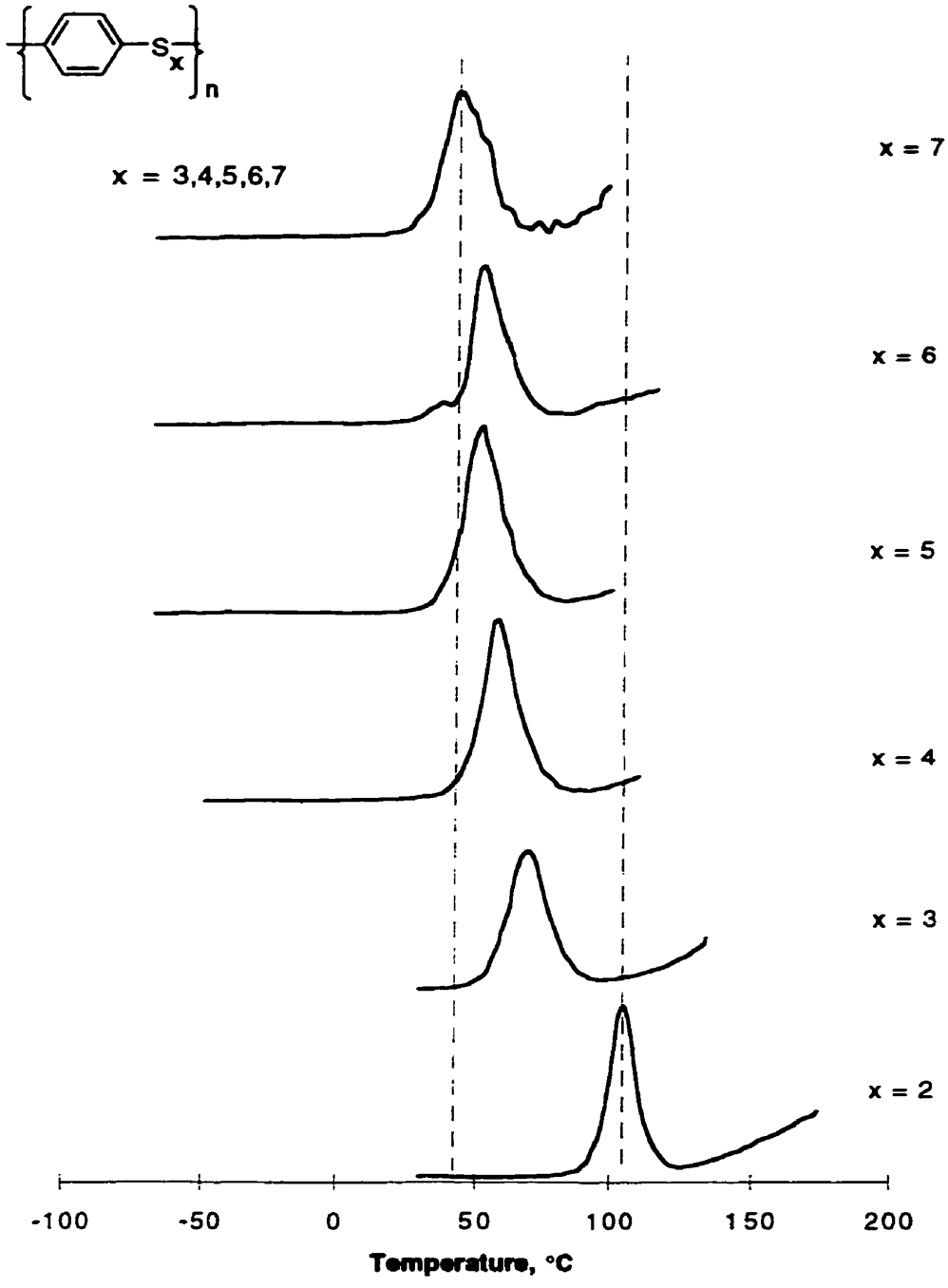


Figure 4.4. Loss tangents (tan δ) of polysulfanes **3.2** obtained from melt copolymerization reactions.

Experiments were carried out only at 200 °C since this is the optimal temperature for melt ring-opening polymerization and melt copolymerization of cyclic(disulfide) oligomers. A reaction time of 2 hours was used in these copolymerization reactions. The resulting polymers were studied by DSC, TGA and DMTA. T_gs of polysulfanes **4.2** with different numbers of sulfur linkages are shown in Table 2. With the increase in sulfur content, the T_gs decrease. Poly(disulfide) **4.2** prepared by melt ring-opening polymerization has a T_g of 84 °C, while the polysulfane **4.2** with x = 7 has a T_g of only 12 °C. The T_g of polysulfur obtained by the quenching of molten sulfur is -30 °C.[8] Similar to polysulfur, polysulfane **4.2** with x = 7 is a rubber, which has very good solvent resistance. It is insoluble in common organic solvents, such as $CHCl_3$, THF, NMP, DMAc, etc. The resulting material stays as a rubber after standing at room temperature for one year, which indicates the sulfur linkages in the polymer chain are very stable. The presence of the phenylene group thus contributes to the higher T_gs for polysulfanes **4.2** compared with polysulfur. Loss tangents (tan δ) obtained from DMTA studies show the same trend (Figure 4.4 and Table 4.2). The loss tangents listed in Table 4.2 are from experiments performed at 1 Hz. The poly(disulfide) obtained by a melt ring-opening polymerization reaction of cyclic(disulfide) oligomers **3** has a tan δ of 108 °C, while polyarylsulfane **4.2** with x = 7 has a tan δ of only 44 °C. Poly(disulfide) **4.2** has the highest thermal stability according to the TGA data with a 5 % weight loss at 459 °C. Polysulfane **4.2** with x = 7 has a 5 % weight loss at 249 °C. From x =2 to x = 3, T_g decreased 34 °C, tan δ decreased 35 °C and the temperature for 5 % weight loss decreased 117 °C.

4.6. Conclusions

Free radical copolymerizations of cyclic(arylene disulfide)s and elemental sulfur were successfully carried out in the melt. Cyclic(disulfide) oligomers **2.14e** can form high molecular weight polysulfanes with an average of sulfur linkages of 3, 4, 5, 6, and 7 via copolymerization with S_8. The polymers obtained by reaction of cyclic(disulfide) oligomers **2.14e** with S_8 were studied by GPC and NMR, while the reactions between cyclic(disulfide) oligomers **2.14a** were studied by DSC, TGA and DMTA techniques since the latter reactions give insoluble polymers. The formation of copolymers with a range of sulfur linkages for polysulfane **4.2** is confirmed from the

changing of T_g and tan δ. With increasing sulfur contents in polysulfane **4.2**, T_g and tan δ decrease.

4.7. Experimental section

Measurements

Gel permeation chromatography (GPC) analyses were performed on a Waters 510 HPLC. Four consecutive 5 μ phenolgel columns (one linear and three 500 Ä) were used. The eluent was $CHCl_3$ and the UV detector was set at 254 nm. Differential scanning calorimetry (DSC) was carried out on a Perkin-Elmer DSC-7 thermal analysis system at a heating rate of 10 °C/min and the mid points of the transitions were taken as the T_g. ^{13}C-NMR spectra were recorded on a Varian UNITY500 NMR instrument and $CDCl_3$ was used as reference. Dynamic mechanical property measurements were carried out on a Polymer Laboratories Dynamic Mechanical Thermal Analyzer (DMTA). The storage moduli (E'), loss moduli (E"), and loss tangents (tan δ) were obtained in the dual cantilever bending mode as a function of temperature, over the range of -50 °C to 150 °C. The heating rate was 2 °C/min. The experiments were performed at three frequencies (0.3, 1, 10 Hz) under N_2 atmosphere.

Materials

Cyclic(arylene disulfide) oligomers **2.14a** and **2.14e** were prepared from 4,4'-thiobis(benzenethiol) and 4,4'-isopropylidene bis(benzenethiol) by copper-amine catalyzed oxidation as reported previously.[9] Sublimed powdered sulfur and highly purified diphenyl ether were purchased from Aldrich Chemical Inc. and used as received.

General procedure for solution copolymerization of elemental sulfur with cyclic(disulfide) oligomers 2.14e

Cyclic(disulfide) oligomers **2.14e** (0.100 g, 0.39 mmol based on the repeating unit), diphenyl ether (0.500 g) and the designated amount of sulfur were mixed together and charged in a Pyrex test tube (1.5 x 15 cm), which was capped with a septum and a slow flow of N_2 was allowed to pass through. The test tube was immersed in a salt bath preheated to a specific temperature and aliquots were taken from time to time for GPC analysis.

General procedure for melt copolymerization of elemental sulfur with cyclic(disulfide) oligomers 2.14e

Cyclic(disulfide) oligomers **2.14e** (0.100 g, mol) and the calculated amount of elemental sulfur were thoroughly mixed together. The sample mixture (~ 10 mg) was placed in a DSC aluminum pan, covered with an aluminum cover to prevent the loss of elemental sulfur because of sublimation, and heated under N_2 atmosphere with a flow rate of 200 mL/min on a Seiko 220 TGA/DTA instrument. After cooling down, either NMR or GPC analysis was performed on the resulting materials.

General procedure for melt copolymerization of elemental sulfur with cyclic(disulfide) oligomers 2.14a

The mixture (0.500 g) of cyclic(disulfide) oligomers **2.14a** and elemental sulfur was placed on a piece of aluminum foil and the foil was folded into approximately a 2 x 3 cm plate. The plate was put on a hot plate with the surface temperature preset at 200 ℃ for 2 h. The aluminum foil was removed and the polymers were subjected to analysis. For DMTA testing, the polymers (0.300 g) were heated to a temperature range of ca. 200 ℃ and a pressure of *ca.* 20 MPa was applied for 5 min. The dimensions of the rectangular blocks molded for the bending mode experiments were typically 2.0 x 6.0 x 30.0 mm.

Quantative determination of the amounts of free sulfur in reaction mixtures

Specific amounts of diphenyl ether and sulfur were carefully weighed and dissolved in $CHCl_3$ and the resulting solutions were used to calibrate the GPC instrument. A stock solution of diphenyl ether in $CHCl_3$ (14.8000 g) was prepared from 1.0844 g of diphenyl ether. For each GPC sample (weighed with analytical balance), about 50 mg (weighed with analytical balance) of the stock solution was first added and then diluted with $CHCl_3$. The resulting mixture was shaken for 2 h on an electric shaker prior to GPC analysis. The amounts of free sulfur were then calculated based on the resulting GPC data.

4.7. References and notes

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Chapter 5. Preparation of Poly(thioarylene)s from Cyclic(arylene disulfide) Oligomers

5.1. Introduction

The synthesis of poly(thioarylene)s has been extensively studied, since poly(thio-1,4-phenylene) (PPS) is an excellent high-performance semicrystalline thermoplastic with outstanding thermal, oxidative and chemical resistance. poly(thioarylene)s are generally prepared by the condensation of dichloroaromatic compounds with sodium sulfide in N-methylpyrrolidinone (NMP).[1-4] In recent years, several new synthetic methods have been developed. Oxidative polymerization of diaryl disulfides has been extensively studied by Tsuchida et al.[5,6] In addition, poly(thioarylene)s have been synthesized *via* electrophilic substitution reactions utilizing arylalkylsulfides[7], methylphenylsulfoxide,[8] and sulfur chloride.[9] However, the use of large amount of strong acids in all of these reactions is a major drawback. Fagerburg *et al.* have developed a melt process for preparation of poly(thioarylene)s by reaction between sulfur and diiodo compounds. This process has been reported in several patents and papers.[10-15] The diiodo compounds can be prepared by reaction of iodine with aromatic compounds in the presence of oxygen generating water as the byproduct,[16] therefore, the iodine can be recycled. The products contain significant amount of disulfide linkages and a method for removal of these linkages has been patented.[17] poly(thioarylene)s have also been prepared by reduction of the soluble precursor poly(arylene sulfoxide)s.[18-20] Transition-metal activated dichlorobenzene was used by Dembek to prepare soluble poly(thioarylene) precursors,[21] however, the demetallation method needs improvement. Several research groups have studied the melt ring-opening polymerization of cyclic(arylene thioether) oligomers.[22-27] Although a more feasible and economical preparation of cyclic oligomers is required, this process provides the possibility of easy material processing, since the cyclic oligomers have much lower melt viscosities compared to the linear high molecular weight polymers. The polymerization of bis(haloaryl disulfide)s in diphenyl ether solution was reported in 1991.[28,29] PPS obtained using this method after annealing had a T_m of 313°C.[30]

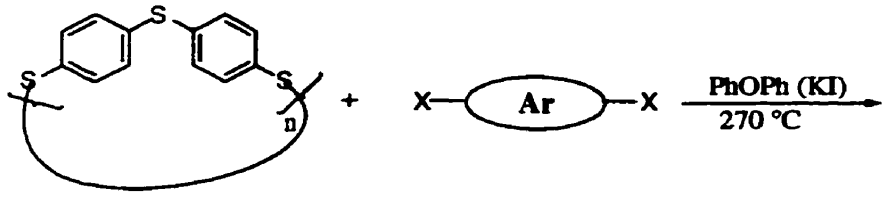
5.2. Strategy and goals

A series of cyclic(arylene disulfide) oligomers have been prepared by oxidative coupling of dithiols with oxygen using a copper-amine catalyst. The cyclic(arylene disulfide) oligomers undergo melt ring-opening polymerization to give high molecular weight poly(arylene disulfide)s by a free radical mechanism. Since the thermal reaction of bis(4-iodophenyl) disulfide gave high molecular weight PPS, [28,29] we envisaged that high molecular weight PPS can be prepared from the reaction of cyclic(disulfide) oligomers derived from 4,4'-thiobis(benzenethiol) and a 1,4-dihalobenzene. This method should provide a convenient way to prepare some poly(thioarylene)s. It is the objective of this chapter to describe detailed studies of this novel process and the preparation of some novel poly(thioarylene)s.

5.3. Synthesis of PPS from cyclic(disulfide) oligomers 2.14a.

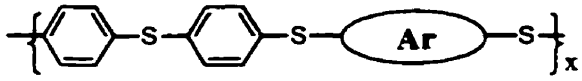
The polymerization reaction is shown in Scheme 5.1. Throughout this chapter , **5.3.1a-h** is used to represent the polymers prepared from diiodo compounds, while **5.3.2a-h** is used to represent the polymers prepared from dibromo compounds. The cyclic(disulfide) oligomers **2.14a** used here have a number-average molecular weight M_n of 380 and a weight-average molecular weight M_w of 570 as determined by GPC (using polystyrene standards). The synthesis of poly(*p*-phenylene sulfide) (PPS) from cyclic(disulfide) oligomers **2.14a** was first carried out. Because of the insolubility of PPS, the polymers formed were only examined by differential scanning calorimetry. The relationships between molecular weight and thermal properties have been established although they are probably not reliable.[15] No glass transition temperature T_g was observed for any of the PPS polymers during the first heating scan. After quenching the samples, a T_g, a crystallization temperature T_c, and a melting point T_m were observed. At the beginning, it was expected that stoichiometric amounts of **2.14a** and 1,4-diiodobenzene (**5.1a**) would be required to obtain PPS with the highest molecular weight. However, with stoichiometric amounts, PPS with a glass transition temperature of 85 ℃ was obtained. It was found that an excess amount of **5.1a** is required to obtain PPS with higher glass transition temperatures. The effects of molar ratios of reactants on thermal properties of PPS is shown in Table 5.1. Although the glass transition temperature should be a monotonic function of molecular weight, we had difficulty in choosing the better condition between entry 3 and entry 4 in Table 5.1 since the difference of T_g is small. T_c is also a monotonic function of molecular weight, and it has much larger changes than T_g.[15] Although it may not be

suitable to use the correlation equation from the reference directly to polymers synthesized by the

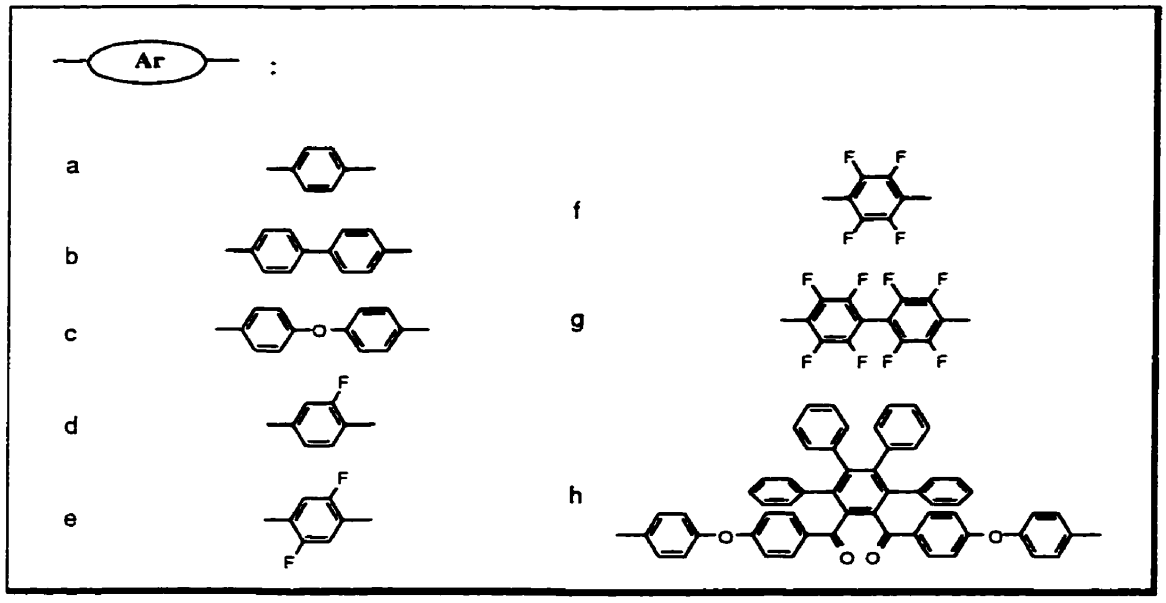


2.14a

5.1 X = I
5.2 X = Br



5.3



Scheme 5.1. Synthesis of poly(thioarylene)s from cyclic(disulfide) oligomers **2.14a**

present preparation method, the trend should be applicable, i.e., the higher the T_c detected by DSC, the higher the molecular weight for a series of polymers prepared by the same method using consistent measurements. The data in Table 5.1 shows that the molar ratio of cyclic(disulfide) oligomers **2.14a** to 1,4-diiodobenzene has a significant influence on the T_c of the product. 1,4-Diiodobenzene has to be used in ~4% excess to obtain PPS with the highest T_c, which we assume represents the highest molecular

weight according to the above arguments. Presumably, this is due to the decomposition of the diiodo compound at high temperatures. The need for excess diiodo compounds has been rationalized by other researchers in other polymerization reactions.[31] However, when 1,4-dibromobenzene was used, the molar ratio of 1:1 of the reactants was found to be optimum. The PPS obtained after 24h reaction has a T_c of 150 °C, a T_g of 92 °C, and a T_m of 275 °C .

Table 5.1. Effect of molar ratio of reactants on thermal properties of PPS

No.	Yield (%)[a]	**5.1/2.14a**	T_g(°C)[b]	T_c(°C)[b]	T_m(°C)[b]
1	97	1.00	85	123	284
2	98	1.01	85	125	286
3	94	1.02	88	127	287
4	97	1.04	88	132	286
5	96	1.06	82	125	286

a. Based on the amount of **2.14a**.

b. Measured by DSC under nitrogen atmosphere at a heating rate of 20 °C/min. All the reported data were obtained by scanning of the quenched samples.

High temperature GPC analysis showed that polymer in entry 4 in Table 5.1 has a weight average molecular weight of 15,200 and a number average molecular weight of 5,300 using polystyrene standards. The PPS obtained from 1,4-dibromobenzene has a M_w of 19,600 and a M_n of 6,900.

The structure of PPS prepared by the present method was studied by IR and solid state ^{13}C-NMR. The FT-IR spectra (KBr) of PPS **5.3.1a** and **5.3.2a** are identical. Both of them show strong absorptions at 814 cm^{-1} attributed to 1,4-substituted phenylene, which confirmed that they have linear, 1,4-phenylene sulfide structures (Figure 5.1). There is no visible absorption peak at 1234 cm^{-1} (-C-O-C-)

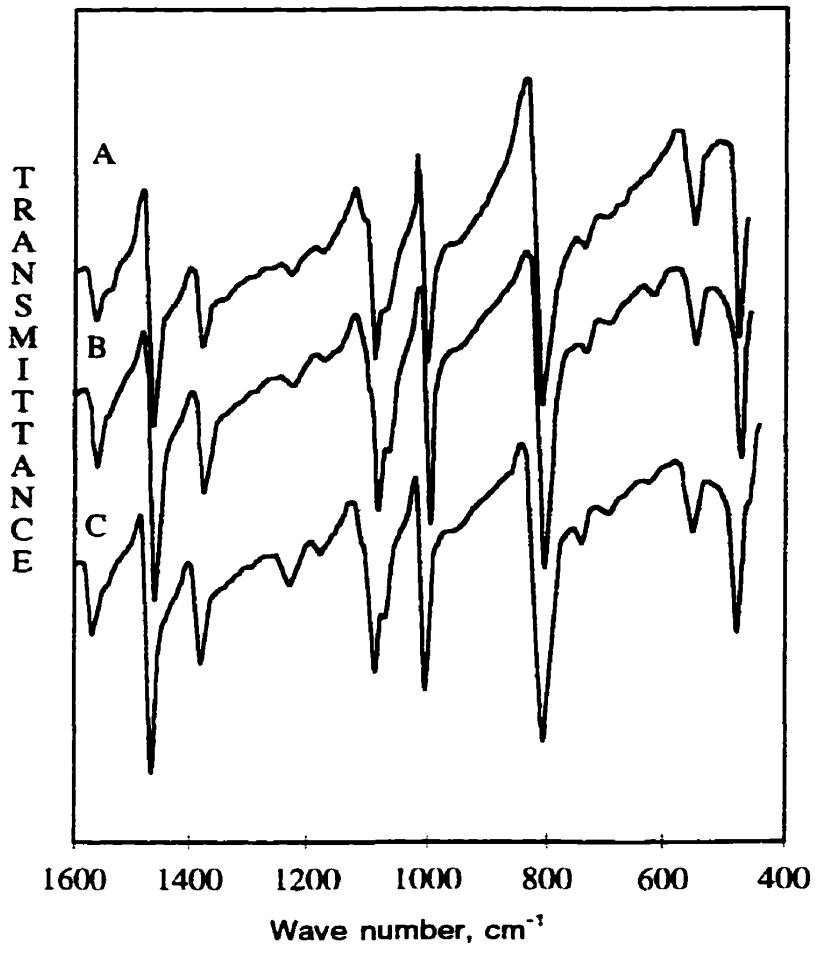


Figure 5.1. FT-IR spectra of PPS polymers. (A). Commercial PPS; (B). PPS from 1,4-dibromobenzene; (C). PPS from 1,4-diiodobenzene.

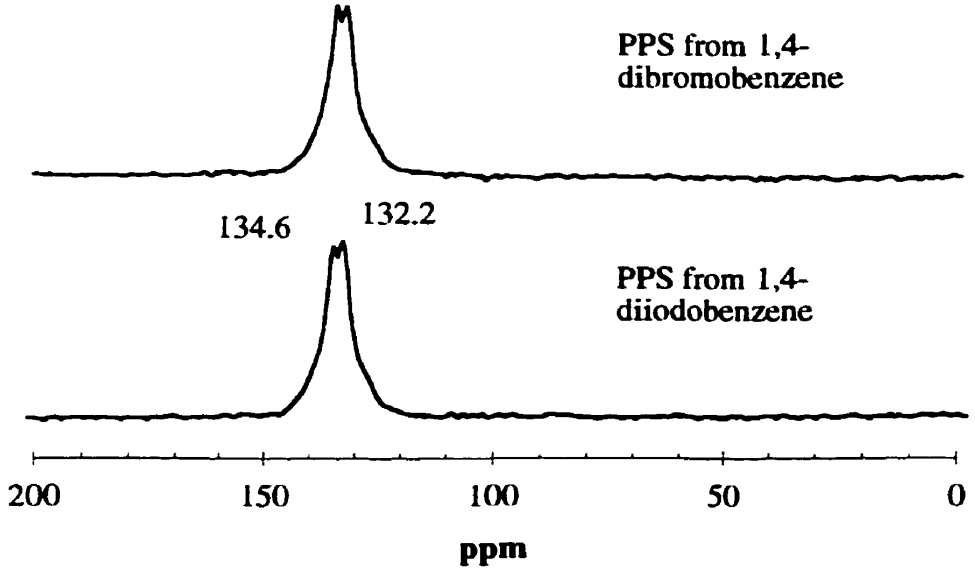
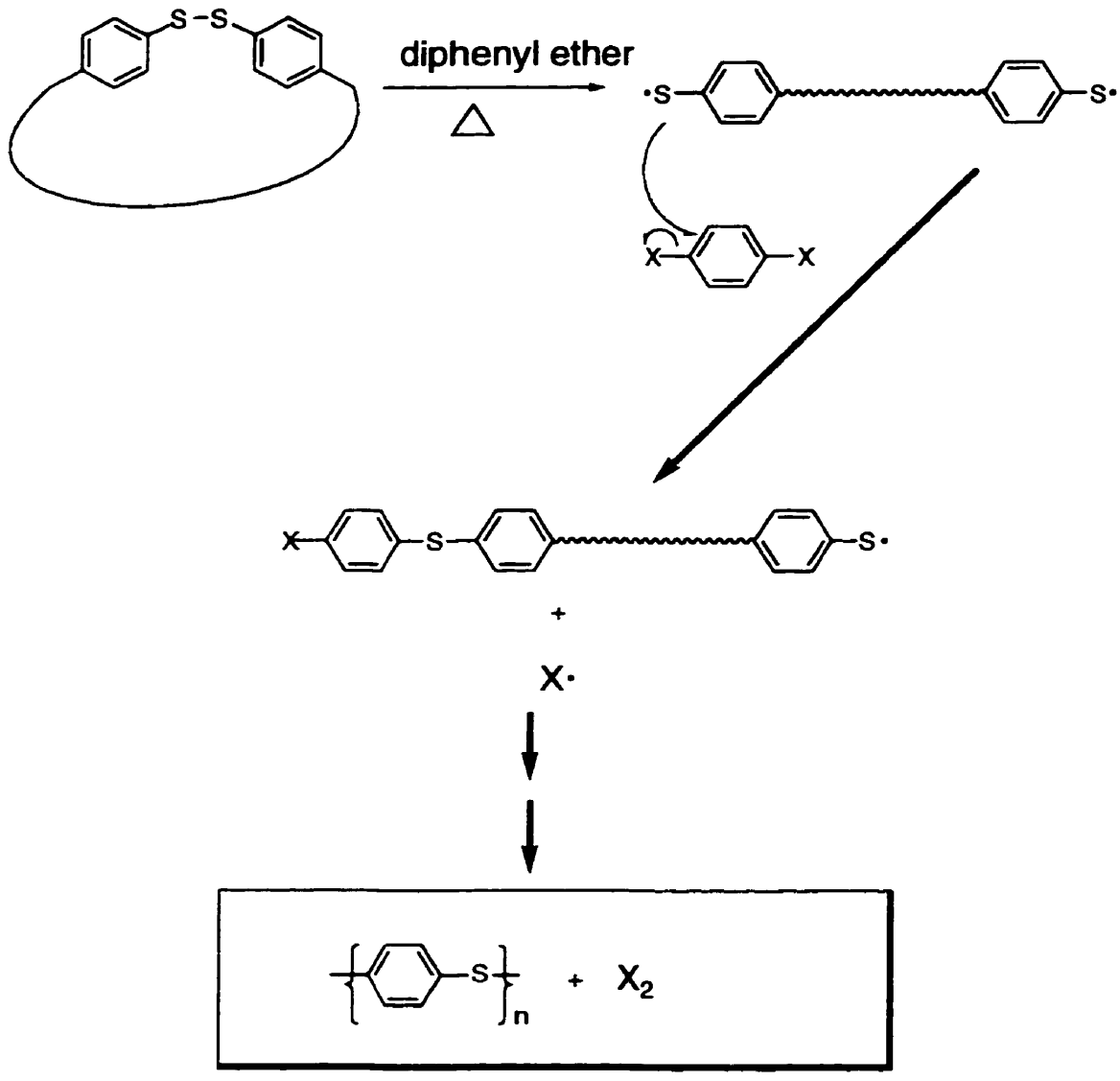


Figure 5.2. Solid state ^{13}C-NMR of PPS polymers

for PPS **5.3.2a**, which was apparent when the polymerization was carried out in the absence of potassium iodide.[28,29] The solid state ^{13}C-NMR spectra of both PPS **5.3.1a** and **5.3.2a** are identical and show two peaks at 134.6 and 132.2 ppm, which are in accordance with the reported results (Figure 5.2).[28]



Scheme 5.2. Proposed mechanism for polymerization reaction between cyclic(disulfide) oligomers and dihalocompounds

A proposed polymerization mechanism is illustrated in Scheme 5.2, and is a typical free-radical *ipso*-substitution reaction. At high temperatures, disulfide linkages

in cyclic(disulfide) oligomers are ruptured and give thiyl radicals. The thiyl radicals *ipso*-substitute the halogen atom and form diphenyl sulfide linkages and halogen radicals. The iodine radicals combine to form iodine which distills from the reaction mixture. However, the bromine radicals are very reactive and brominate the solvent diphenyl ether which destroys the stoichiometric balance of reactants so that high molecular weight polymer is not formed. Potassium iodide serves as a reductant for the bromine atoms to suppress the side reactions caused by the reactive bromine radical and makes the use of dibromo aromatic compounds as monomers practical.

5.4. Synthesis of poly(thioarylene)s from cyclic(disulfide) oligomers.

Table 5.2. Thermal properties of poly(thioarylene)s

Polymers	Yield (%)[a]	T_g(°C)[b]	T_c(°C)[b]	T_m(°C)[b]	TGA (°C)[c]
5.3.2b	97	115	-	-	500
5.3.2c	96	85	139	238	493
5.3.2h	92	192	-	-	525
5.4.1a	83	146	230	295	520
5.4.2b	92	-	-	454[d]	496
5.4.2c	93	124	178	261	510

a. Based on the amounts of cyclic(disulfide) oligomers.

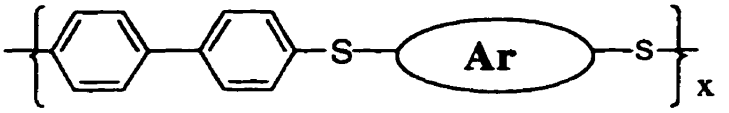
b. Measured by DSC under nitrogen atmosphere at the heating rate of 20 °C/min. All the reported data were obtained by scanning of the quenched samples.

c. Temperatures for 10% weight loss, which were measured under nitrogen atmosphere at a heating rate of 20 °C/min.

d. Obtained from the first heating scan. The second heating scan was not performed because of decomposition of the sample.

By applying the polymerization conditions described above, a series of poly(thioarylene)s were prepared from cyclic(disulfide) oligomers **2.14a**, **2.14c** and different dihaloaromatic compounds. Generally, 4% excess of diiodo compounds

were used, while equivalent amounts of dibromo compounds were used. Most of the polymers are insoluble in common organic solvents (except **5.3.2c**), therefore we do not have a direct measurement of molecular weights. All of the polymers were obtained in very high yields.



5.4

The thermal propertiers of the polymers are listed in Table 5.2. Polymer **5.3.2c** has the same glass transition temperature T_g as commercial PPS. However, the melting point is much lower than that of PPS due to the presence of ether linkages. It is interesting to note that this polymer has much higher (~50 °C) melting point than poly(thio-1,4-phenyleneoxy-1,4-phenylene) (T_m = 191 °C).[32] As shown in Figure 5.3, in all cases, polymers containing both thioether and ether linkages have lower melting points than PPS and poly(oxy-1,4-phenylene).[33] Poly(biphenyl sulfide) **5.4.2b** is a highly crystalline polymer and has a melting point of 454 °C. This polymer has been previously prepared by reacting difluorobiphenyl or dibromobiphenyl with a alkali metal sulfide in NMP.[34,35] Polymer **5.4.2b** shows almost the same melting point as that prepared from difluorobiphenyl and sodium sulfide (445 °C),[34] while the melting point is much higher than that reported in another paper (387 °C),[35] however, these materials are believed to be low molecular weight oligomers. Polymers **5.3.2b** and **5.4.1a** can be viewed as the copolymer of PPS and poly(thiobiphenylene) with molar ratio of 2:1 and 1:1, respectively. Comparing with the results reported by Park *et al.*,[35,36] the polymers prepared by the present method have much higher glass transition temperatures, which indicates that the polymers prepared by the present method are higher molecular weights. Polymer **5.3.2h** is an amorphous polymer, which is readily soluble in normal organic solvents, such as chloroform, THF. The number average molecular weight of **5.3.2h** was 11,000, and the weight average molecular weight was 29,000 as determined by GPC using polystyrene standards. If only a very small amount of solvent diphenyl ether was used, polymers with very broad molecular weight distribution were obtained,

which indicates some branching reaction was taking place. This was also the case for the melt polymerization of bis(4-iodophenyl) disulfide.[37]

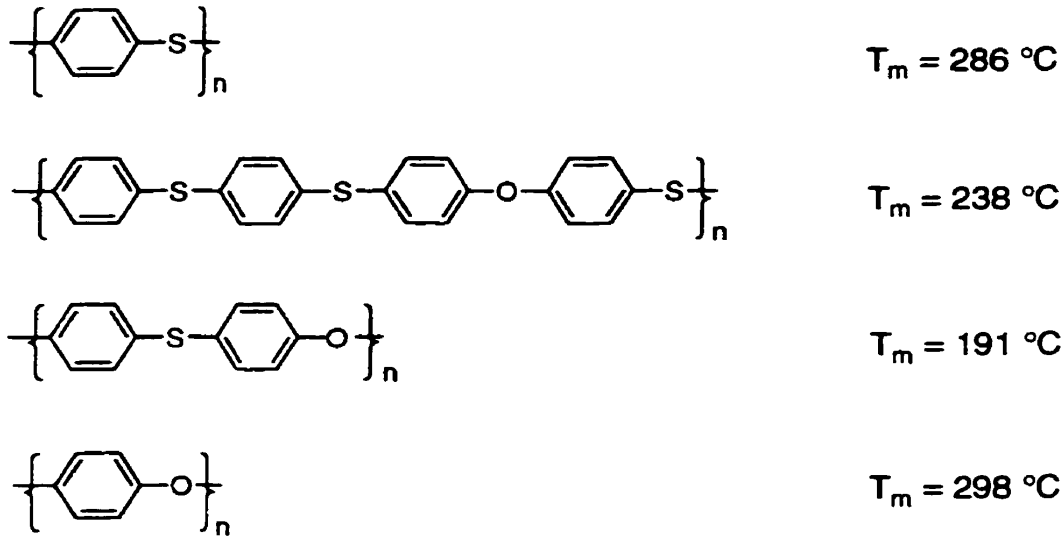


Figure 5.3. Thermal properties of PPS and PPS derivatives

5.5. Synthesis of poly(thioarylene)s from fluorine containing monomers.

It was observed that the fluorine atom is unreactive towards the substitution reaction by thiyl radicals.[28,38] Therefore, it should be possible to prepare fluorinated poly(thioarylene)s by reaction of cyclic(disulfide) oligomers and dibromo or diiodo fluoroaromatic compounds. The study of fluorinated polymers has received extensive attention, since the introduction of fluorine into polymers can result in significant changes in polymer properties, such as low dielectric constant.[39,40] Several fluorinated poly(thioarylene)s were prepared by the reaction between cyclic(disulfide) oligomers **2.14a**, **2.14c** and fluorinated aromatic compounds at high temperature. The thermal properties of all the polymers prepared are listed in Table 5.3. Polymers **5.3.2d**, and **5.3.2e** are not soluble in normal organic solvents, while polymers **5.3.1f**, **5.3.2f**, **5.4.2f** and **5.4.2g** are soluble in hot chloroform. Polymer **5.3.2g** is soluble in chloroform at room temperature. By examining the thermal properties of polymers **5.3d-g**, it is apparent that the higher the content of fluorine in the polymers, the higher the glass transition temperatures. Although melting points were observed in the first heating scans, only T_gs were observed after quenching the

samples which indicates that fluorinated moieties lower the rate of crystallization. Only low molcular weight polymers were obtained by the present method. The M_n of **5.3.2g** was 3200, and M_w was 6100 as determined by GPC. The thiyl radical is electrophilic and prefers to attack an electron rich aromatic nucleus.[38] Fluorine is a strong electron withdrawing group and significantly decreases the electron densities in the aromatic rings. The more fluorinated the monomer, the lower the reactivity. It is interesting to note that monomer **5.1f** gave a higher molecular weight polymer than monomer **5.2f**, as indicated by the difference of T_gs. This observation indicates that iodinated monomers are preferable for reaction with electron deficient monomers.

Table 5.3. Thermal Properties of fluorinated poly(thioarylene)s

Polymers	Yield (%)[a]	T_g(°C)[b]	T_c(°C)[b]	T_m(°C)[b]	TGA (°C)[c]
5.3.2d	86	86	159	216	510
5.3.2e	84	86	-	-	498
5.3.1f	89	105	-	-	514
5.3.2f	72	94	-	-	498
5.3.2g	81	110	-	-	469
5.4.2f	61	159	-	-	520
5.4.2g	93	143	-	-	504

a. Based on the amounts of cyclic(disulfide) oligomers.

b. Measured by DSC under nitrogen atmosphere at a heating rate of 20 °C/min. All the reported data were obtained by scanning of the quenched samples.

c. Temperatures for 10% weight loss, which were measured under nitrogen atmosphere at a heating rate of 20 °C/min.

5.6. Conclusions

A novel method for the preparation of poly(thioarylene)s from cyclic(arylene disulfide) oligomers and diiodo or dibromo aromatic compounds has been demonstrated. A series of poly(thioarylene)s have been prepared from cyclic(disulfide)

oligomers **2.14a** and **2.14c**, which are derived from 4,4'-thiobis(benzenethiol) and 4,4'-biphenyldithiol, respectively. Diiodo monomers had to be used in excess (~4%) to obtain the highest molecular weight polymers, however, equivalent amounts of dibromo monomers could be used. By reacting with cyclic(disulfide) oligomers **2.14a**, 1,4-diiodobenzene gave PPS with T_g of 88 °C and T_m of 286 °C and 1,4-dibromobenzene gave PPS with T_g of 92 °C and T_m of 275 °C . Fluorinated diiodo- or dibromo- monomers have much lower reactivities towards the thiyl radical substitution reaction and only low molecular weight polymers were obtained. All of the poly(thioarylene)s prepared have very high thermal stabilities as indicated by TGA.

5.7. Experimental Section

Measurements. Differential scanning calorimetry (DSC) was carried out with a Seiko 220 DSC instrument at a heating rate of 20 °C/min under nitrogen atmosphere. Thermogravimetry (TG) was carried out with a Seiko TG/TGA 220 thermal analyzer at a heating rate of 20 °C/min under nitrogen atmosphere. Gel permeation chromatography (GPC) analyses were performed on a Waters 510 HPLC equipped with 5μ phenogel columns (linear, 3x500 Å) arranged in series with chloroform as solvent and a UV detector at 254 nm. NMR data were recorded at 500 MHz on a Varian UNITY 500 NMR instrument and are listed in parts per million downfield from tetramethylsilane. FT-IR spectra were measured with an Analet AQS-18 FTIR spectrometer and data was recorded with an Analet MAP-67 data system. Melting points for monomers were taken on a Fisher-Johns melting point apparatus and the thermometer was uncorrected. Solid state ^{13}C-NMR spectra were recorded on a Chemagnetics CMX-300 spectrometer . High temperature GPC analyses were carried out on a Senshu Kagaku Model VHT-GPC SSC-7000 with a Soma Optics S-3750 UV/vis absorption detector set at 360 nm. Two Shodex AT80M/A columns and an AT-800P column from Showa Denko were installed. 1-Chloronaphthalene was used as the eluent and the flow rate was 1 mL/min. The temperatures of the column oven, the transfer line, and the flow cell were regulated at 210 °C. Polystyrene standards substituted by a fluorescent pyrene group were used as calibrating references.

Materials. Cyclic(disulfide) oligomers **2.14a** and **2.14c** were prepared from 4,4'-thiobis(benzenethiol) and 4,4'-biphenyldithiol by copper-amine catalyzed oxidation.[41] **5.2a**, **5.1a**, **5.2c** and diphenyl ether were purchased from Aldrich Chemical Co. and used without further purification. Commercially available **5.2b**, **5.2d**, **5.2e**, **5.1f**,

5.2f, and **5.2g** were recrystallized from absolute ethanol. 1,2-Bis(4-fluorobenzoyl)-3,4,5,6-tetraphenylbenzene was synthesized according to the previously reported method.[42]

1,2-Bis(4'-bromphenoxybenzoyl)-3,4,5,6-tetraphenylbenzene (5.2h). A 100 mL three neck flask was charged with 10.0 g (16.0 mmol) of 1,2-bis(4-fluorobenzoyl)-3,4,5,6-tetraphenylbenzene, 5.53 g (32.0 mmol) of 4-bromophenol, 8.83g (64.0 mmol) of anhydrous K_2CO_3, 40 mL of DMAc and 8 mL of toluene. The solution was heated to reflux, and water was removed by azeotropic distillation. The reaction mixture was kept at reflux for 5 h, cooled down to room temperature and poured into 400 mL of water. The solid product was filtered and washed with water and then with methanol. The product was recrystallized from toluene/ethanol, giving 14.2 g (95%) of the desired product. mp. 215-217 °C. ^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.60 (d, 4H), 7.43 (d, 4H), 6.89-6.72 (m, 28H); ^{13}C-NMR (125 Mhz, $CDCl_3$) δ 197.27, 160.18, 155.17, 142.00, 139.16, 138.56, 138.48, 137.98, 133.37, 132.64, 131.75, 131.03, 130.84, 126.96, 126.76, 125.4.27, 125.76, 120.93, 117.19, 116.42. FAB-MS *m/e* 933; Elemental analysis, calculated: C 72.11, H 3.89; found: C 72.08, H 3.86.

General procedure for polymerization of cyclic(arylene disulfide) oligomers with diiodo compounds. Cyclic(disulfide) oligomers **2.14a** (0.248 g, 1.0 mmol), diiodoaromatic compond, and diphenyl ether (0.5 mL) were charged in a Pyrex test tube (1.5 x 15 cm) equipped with a mini magnetic stirring bar and a nitrogen inlet. The test tube was immersed in a salt bath preheated to 270 °C to a depth of about 2 cm to cover the contents for 10 h. 1-Chloronaphthalene (3 mL) was then added to dilute the polymer. The solution was poured into 300 mL of methanol to precipitate out the polymer and the polymer was isolated by filtration and washed with hot methanol, hot chloroform and then methanol, respectively. The product was dried at 100 ℃ under vacuum for 24 h and then subjected to analysis.

General procedure for polymerization of cyclic(arylene disulfide) oligomers with dibromo compounds. Cyclic(disulfide) oligomers **2.14a** (0.248 g, 1.0 mmol), dibromoaromatic compound (1.0 mmol), powdered potassium iodide (0.84 g, 5.1 mmol), and diphenyl ether (0.5 mL) were charged in a Pyrex test tube (1.5 x 15 cm) equipped with a mini magnetic stirring bar and a nitrogen inlet. The

test tube was immersed in a salt bath preheated to 270 °C to a depth of about 2 cm to cover the contents inside for 24 h. 1-Chloronaphthalene (3 mL) was added to dilute the polymer. The solution was poured into 300 mL of methanol to precipitate out the polymer. The polymer was isolated by filtration and washed with hot water, hot methanol, hot chloroform and then methanol. The product was dried at 100 °C under vacuum for 24 h and then subjected to analysis.

For the polymerizations of cyclic(disulfide) oligomers with 1,4-dibromo-2,5-difluorobenzene, 1,4-diiodotetrafluorobenzene, and 4,4'-dibromooctafluorobiphenyl, the washing with hot chloroform was either omitted or cold chloroform was used instead since the polymer products are soluble in hot chloroform.

Synthesis of polymer 5.3.2h. Cyclic(disulfide) oligomers **2.14a** (0.248 g, 1.0 mmol), **5.2h** (0.933 g, 1.0 mmol), powdered potassium iodide (0.84 g, 5.1 mmol), and diphenyl ether (3.0 ml) were charged in a Pyrex test tube (1.5 x 15 cm) equipped with a mini magnetic stirring bar and a nitrogen inlet. The test tube was immersed in a salt bath preheated to 260 °C to a depth of about 4 cm to cover the contents for 40 h. After cooling down, 5 mL of chloroform was added to dilute the mixture. The solution was poured into 300 mL of vigorously stirred methanol to precipitate out the polymer. The polymer was dissolved in 20 mL of chloroform and filtered through a thin layer of celite to remove the salt. The solution was concentrated and poured into 200 mL of methanol to precipitate the polymer. After filtration and drying at 100 °C under vacuum for 24 h, 0.944 g of white polymer was obtained. Yield, 92%.

5.8. References and Notes

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Chapter 6. Novel Synthesis of Poly(thioarylene)s *via* Reaction Between Arylthiols and Bromo Compounds with a Free Radical Initiator

6.1. Introduction

The commercial process for the manufacture of poly(2,6-dimethyl-1,4-phenylene oxide) (PPO®), an important engineering plastic, is based on an oxidative polymerization reaction.[1-3] The polymerization of 2,6-dimethylphenol is realized with a copper-amine catalyst in the presence of oxygen. When the same reaction conditions were applied to benzenethiol, only diphenyl disulfide was formed.[4,5] PPO can also be prepared from the sodium salt of 4-bromo-2,6-dimethylphenol by the addition of a catalytic amount of a free radical initiator at room temperature.[6] Much more stringent conditions are required to prepare the homopolymer of benzenethiol, poly(*p*-phenylene sulfide) (PPS), compared to the preparation of PPO. PPS is commercially manufactured by a condensation reaction between *p*-dichlorobenzene and sodium sulfide in a polar solvent, such as N-methylpyrrolidinone at 200 - 280 °C under high pressure.[7,8] Because of its outstanding thermal, oxidative and chemical resistance, the synthesis of PPS has been extensively studied. At least four different methods have been reported for the preparation of PPS. The industrial process proceeds through a nucleophilic substitution reaction.[7] Melt copolymerization of 1,4-diiodobenzene and sulfur,[9,10] thermal polymerization of bis(4-iodophenyl)disulfide[11] and copolymerization of cyclic(arylene disulfide) oligomers with dihaloaromatic compounds[12,13] have been described as proceeding by free radical mechanisms. The polymerization of salts of 4-bromobenzenethiol is believed to be a single-electron transfer process.[14,15] Electrophilic substitution reactions have been extensively studied by Tsuchida.[16-19]

There are two reports which are related to the use of a catalytical process or an initiator for the preparation of PPS. Tsuchida *et al.* reported that high molecular weight PPS was obtained via a soluble precursor by catalytic oxidative polymerization of methyl phenyl sulfide with oxygen in the presence of cerium ammonium nitrate (CAN) catalyst in the presence of strong acid.[20] The major drawbacks of this process are the need for large amounts of strong acids and the necessity for maintaining

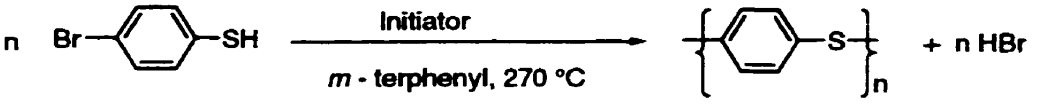
anhydrous conditions. In 1986, Novi *et al.* reported that polymerization of 4-bromobenzenethiolate was achieved in DMSO by the empolyment of catalytic amounts of a diazonium salt *via* a radical-anion chain pathway.[21] Because the polymerizations were carried out at room temperature and PPS is highly insoluble, it is not surprising that only oligomeric PPS was obtained with repeating units around 9 based on the elemental analyses.

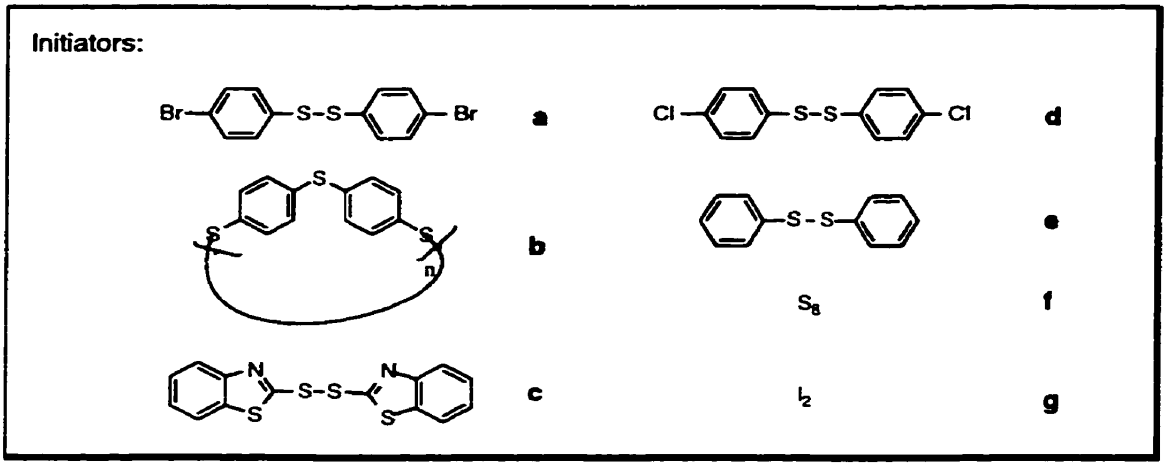
6.2. Strategy and goals

In Chapter 5, we have described the synthesis of poly(thioarylene)s by reacting of cyclic(arylene disulfide) oligomers with dihalocompounds. When dibromocompounds were used, a reducing agent (potassium iodide) had to be used to react with the bromine radicals produced. Since benzenethiol is a stronger reducing agent than potassium iodide, a novel polymerization reaction is possible between arylene dithiols and dibromo aromatic compounds in the presence of free radical initiator. In this chapter, we will describe this novel polymerization reaction, which provides high molecular weght PPS and poly(thioarylene)s without formation of any salt and HBr is formed as the sole side product.

6.3. Homopolymerization of 4-bromobenzenethiol with a free radical initiator.

The polymerization of 4-bromobenzenethiol was achieved when a catalytic amount of free readical initiator was present in the reaction mixture (Scheme 6.1). The polymerization reaction was carried out in *m*-terphenyl solution at 270 °C. *m*-Terphenyl is a high boiling solvent (b.p. 365 °C), which is unreactive to the thiyl radical. It can be easily removed from the products since it is very soluble in hot methanol. The purpose of using a high boiling point solvent is to hold the monomer in solution, since the boiling point of 4-bromobenzenethiol is only 230 °C. Different initiators were used to effect the polymerization reaction, such as bis(4-bromophenyl)disulfide, cyclic(disulfide) oligomers **2.14a**, diphenyldisulfide, 2,2'-dithiobis(benzothiazole), as well as elemental sulfur. Since 4-bromobenzenethiol can be easily transformed to bis(4-bromophenyl)disulfide by oxidants, it is conceivable that catalytic amounts of other oxidants would also be effective initiators for the polymerization reaction.





Scheme 6.1. Polymerization of 4-bromobenzenethiol with different initiators

Bis(4-bromophenyl)disulfide was used as an initiator to determine suitable conditions for the polymerization of 4-bromobenzenethiol. The effect of different conditions on the polymerization are shown in Table 6.1. When 1 mol % of bis(4-bromophenyl)disulfide was used, the molecular weight of the PPS increased as the reaction time increased based on the increasing glass transition temperatures (T_g) and crystallization temperatures (T_c) for the products obtained as measured by differential scanning calorimetry (DSC). Fagurburg *et al.* have established that T_c linearly increases with the logarithm of the degree of polymerization.[22] Although this relationship can not be rigorously applied to PPS polymers prepared by other methods, the trend should be the same. When different amounts of initiator were used for the polymerization carried out for 96 hours, 1 mol % of initiator gave the best result based on both T_g and T_c of the polymer formed. Using 0.5 mol % of initiator, a relatively high molecular weight PPS was isolated although the yield was only 61 %. This is the same phenomena observed for the polymerization of salts of 4-bromobenzenethiol,[23,24] which was termed "preferential polymer formation".[23] As the amounts of initiator were increased, molecular weights of the resulting polymers were lower.

Table 6.1. Polymerization of 4-bromobenzenethiol initiated by bis(4-bromophenyl)disulfide[a]

No.	Cat.% (mol)	Time (h)	Yield (%)	T_g (°C)	T_c (°C)	T_m (°C)
1	1.0	24	93	68	117	259
2	1.0	48	96	75	121	282
3	1.0	72	96	83	133	283
4	1.0	96	95	92	145	285
5	0.5	96	61	79	121	282
6	2.0	96	100	85	138	278
7	3.0	96	96	63	110	261

a. Thermal properties were obtained by DSC at a heating rate of 20 °C/min. Samples were quenched from 350 °C on a cold metal block.

The effects of different initiators on the properties of polymers, obtained by using 1 mol % initiator and 96 hours reaction time, are listed in Table 6.2. Several aryl disulfides were used as effective initiators for the polymerization of 4-bromobenenethiol. In all cases, flexible PPS films were obtained by the following simple technique. PPS powder (200 mg) was put on a piece of aluminum foil and the foil was folded into a rectangle around 1 x 2.5 cm. The rectangle was put on the surface of a hot plate preheated to 330 °C for 5 min and pressed with a piece of glass, then quenched immediately by dipping into cold water. After removing the aluminum foil, a flexible PPS film was obtained.

Based on the T_g and T_c of the products, bis(4-bromophenyl)disulfide as an initiator gave the best results. Bis(4-bromophenyl)disulfide itself is a monomer for PPS under the conditions applied here, hence it would not act as a termination agent.

Elemental analyses for polymers from polymerization reactions initiated by bis(4-bromophenyl)disulfide and cyclic(arylene disulfide) oligomers **b** are listed in Table 6.3. By assuming both of the end groups are bromine atoms, the calculated repeating units for PPS formed by initiation with bis(4-bromophenyl)disulfide is 101

and for PPS initiated by **b** is 92. The weight average molecular weight (M_w = 19600) and number average molecular weight (M_n = 6900) were obtained from high temperature GPC for PPS initiated by **a**. For PPS initiated by **b**, M_w = 15200 and M_n = 5200 were obtained. The GPC chart of PPS obtained from 4-bromobenzenethiol initiated by bis(4-bromophenyl)disulfide is shown in Figure 6.1.

Table 6.2. Polymerization of 4-bromobenzenethiol with different initiators

Catalyst [a]	Yield (%)	T_g(°C) [b]	T_c(°C) [b]	T_m(°C) [b]
a	96	92	146	285
b	96	87	133	284
c	89	89	142	278
d	93	89	143	281
e	96	82	126	277
f	89	87	137	280
g	70	-	-	250

a. The amount of initiator used was 1 mol %. The structures of the initiators are shown in Scheme 6.1.

b. Thermal properties were obtained by DSC at a heating rate of 20 °C/min. Samples were quenched from 350 °C on a cold metal block.

Table 6.3. Elemental analyses and high temperature GPCs for PPS polymers

PPS	Initiator	Elemental Analysis				GPC [a]	
		C	H	S	Br	M_w	M_n
1	**a**	66.21	3.85	29.59	1.46	19,600	6,900
2	**b**	66.83	3.98	30.47	1.60	15,200	5,200

a. The eluent was 1-chloronaphthalene. Polystyrenes were used as calibration standards.

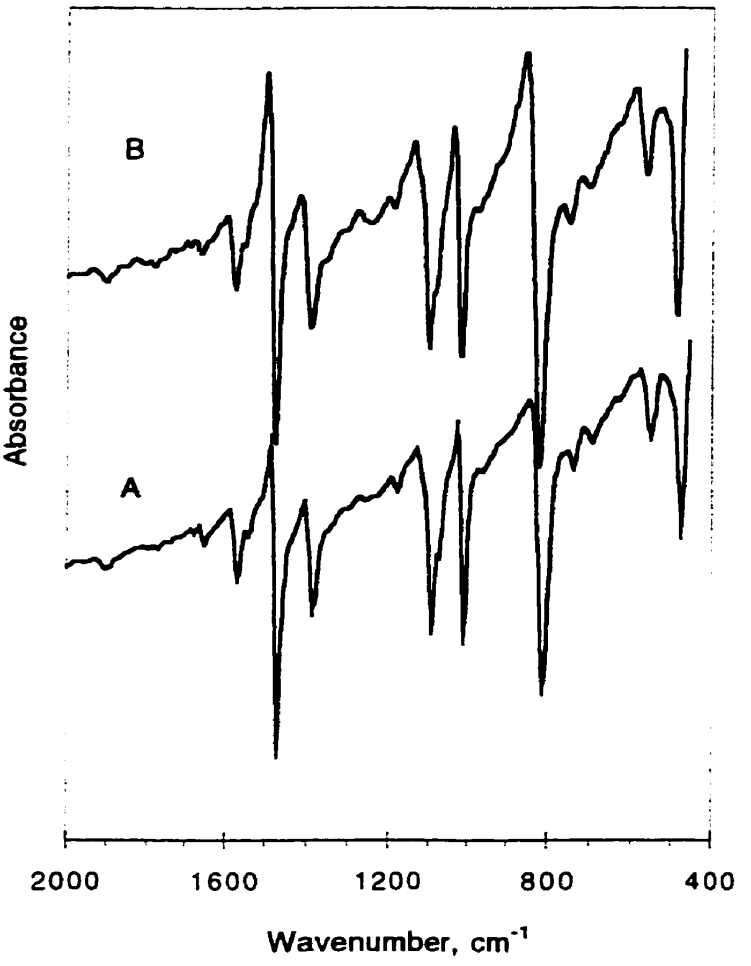


Figure 6.1. FT-IR spectra of PPS polymers. (A). Initiated by cyclic(disulfide) oligomers, **2.14a**; (B). Initiated by **a**.

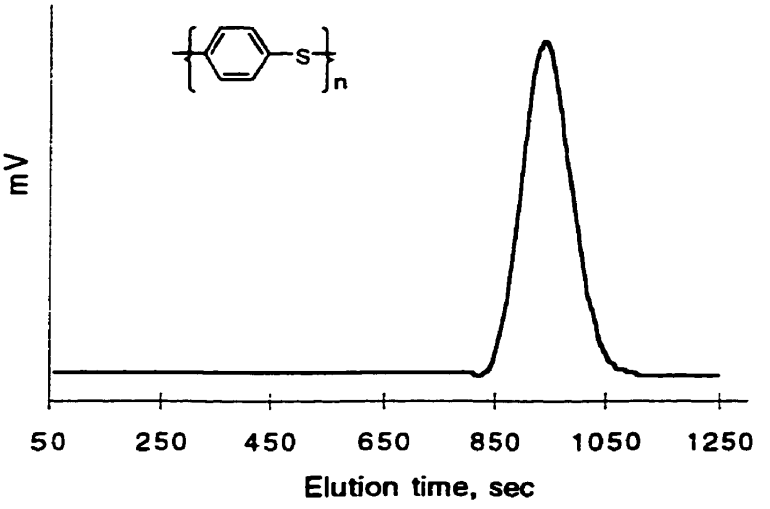


Figure 6.2. High temperature GPC chart of PPS obtained from initiation by **a**

The empirical formula for PPS **1** is $C_{6.0}H_{4.1}S_{1.0}Br_{0.02}$, and for PPS **2** is $C_{5.9}H_{4.2}S_{1.0}Br_{0.02}$. These empirical formula indicate that PPS obtained from polymerization of 4-bromobenzenethiol initiated by bis(4-bromophenyl)disulfide does not contain any significant amount of disulfide linkages. However, PPS initiated by cyclic(arylene disulfide) oligomers may contain small amounts of disulfide linkages. Therefore, bis(4-bromophenyl)disulfide is strongly recommended as the initiator of choice for the polymerization of 4-bromobenzenethiol. When iodine was used as an initiator, only very low molecular weight oligomers were obtained. This is presumably due to the high reduction capability of HI which would terminate the chain reaction.

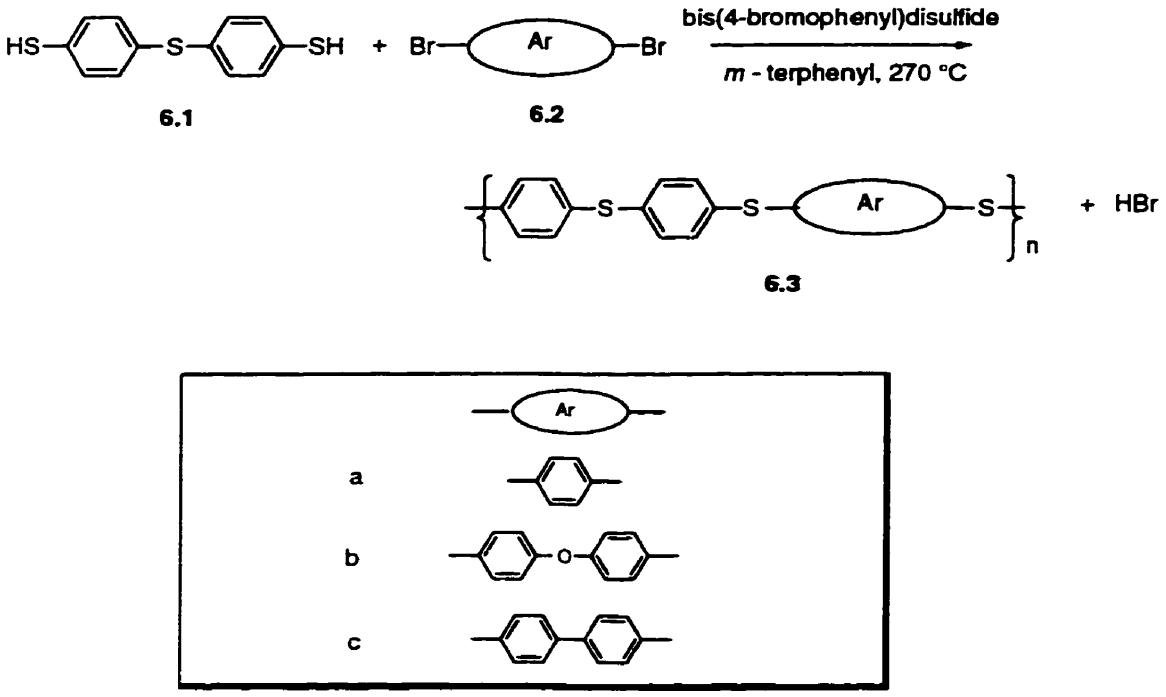
The polymers obtained from polymerization of 4-bromobenzenethiol have been analyzed by FT-IR (Figure 6.2). All of the polymers obtained show IR spectra identical to those of PPS obtained by other methods.[9,25]

Polymerization reactions were also attempted with 4-chlorobenzenethiol. When 1.0 mol % of **b** was used as an initiator, only low molecular weight PPS oligomers with T_g of 55 °C, T_c of 97 °C and T_m of 270 °C were obtained. This low efficacy of the polymerization compared to 4-bromobenzenethiol is due to the low reactivity of the aryl chloride and the very high reactivity of chlorine radical intermediates.

6.4. Copolymerization of aryl dithiols with dibromo arylenes.

4-Bromobenzenethiol is an AB type monomer. This free radical initiated polymerization can also be extended to AA, BB type monomers. 4,4'-Thio-bis(benzenethiol), was chosen to demonstrate the polymerization reaction. 1,4-Dibromobenzene, bis(4-bromophenyl)ether and 4,4'-dibromobiphenyl were used as comonomers. The polymerization reaction is shown in Scheme 6.2. The amount of initiator used was 2.0 mol % and the reaction time was 96 hours and the polymerizations were carried out at 270 °C. The polymers obtained were characterized by DSC and the thermal properties are listed in Table 6.4. All of the polymers are insoluble in common organic solvents, but all are soluble in chloronaphthalene at 200 °C. PPS obtained by this copolymerization reaction has a very high T_g (92 °C), which indicates the polymer has high molecular weight. Polymer **6.3b** has a T_g of 83 °C, which is comparable to that of polymer prepared from cyclic arylene disulfide oligomers **2.14a** and bis(4-bromophenyl)ether.[13] The FT-IR (KBr) spectrum of this polymer shows a strong absorption at 1234 cm^{-1}, which is attributed to stretching of -C-O-C- bonds. Polymer **6.3c** has a T_g of 113 °C, which is higher than that reported

by Park *et al.*,[26,27] while it is comparable to that of polymer prepared from cyclic(disulfide) and 4,4'-dibromobiphenyl.[13]

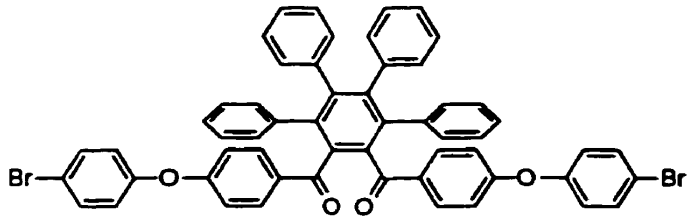


Scheme 6.2. Copolymerization reactions between arylenedithiol **6.1** and dibromo compounds

Table 6.4. Copolymerizations of 4,4'-thiobis(benzenethiol) with dibromo compounds initiated with bis(4-bromophenyl)disulfide

Polymer	Yield (%)	T_g(°C)	T_c(°C)	T_m(°C)
6.3a	90	92	137	271
6.3b	90	83	155	223
6.3c	97	113	-	-

a. Thermal properties were obtained by DSC at a heating rate of 20 °C/min. The samples were quenched from 350 °C on a cold metal block.



5.3h

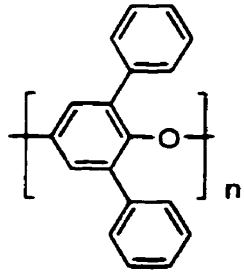
+ 6.1

bis(4-bromophenyl)disulfide
m-terphenyl, 270 °C
Dark red oligomers

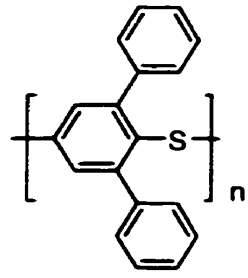
Scheme 6.3. Attempted polymerization between an arylenedithiol and a ketone containing monomer

Attempts to copolymerize 4,4'-thiobis(benzenethiol) with **5.3h** were unsuccessful (Scheme 3), although the intended polymer was previously obtained from copolymerization of cyclic(disulfide) oligomers **2.14a** and **5.3h**.[13] In this case, dark red oligomers were isolated. Apparently, there are some side reactions between the dithiol and ketone groups in **5.3h**, which prevents the formation of polymer.

6.5. Attempted polymerization of 4-bromo-2,6-diphenylbenzenethiol



6.4

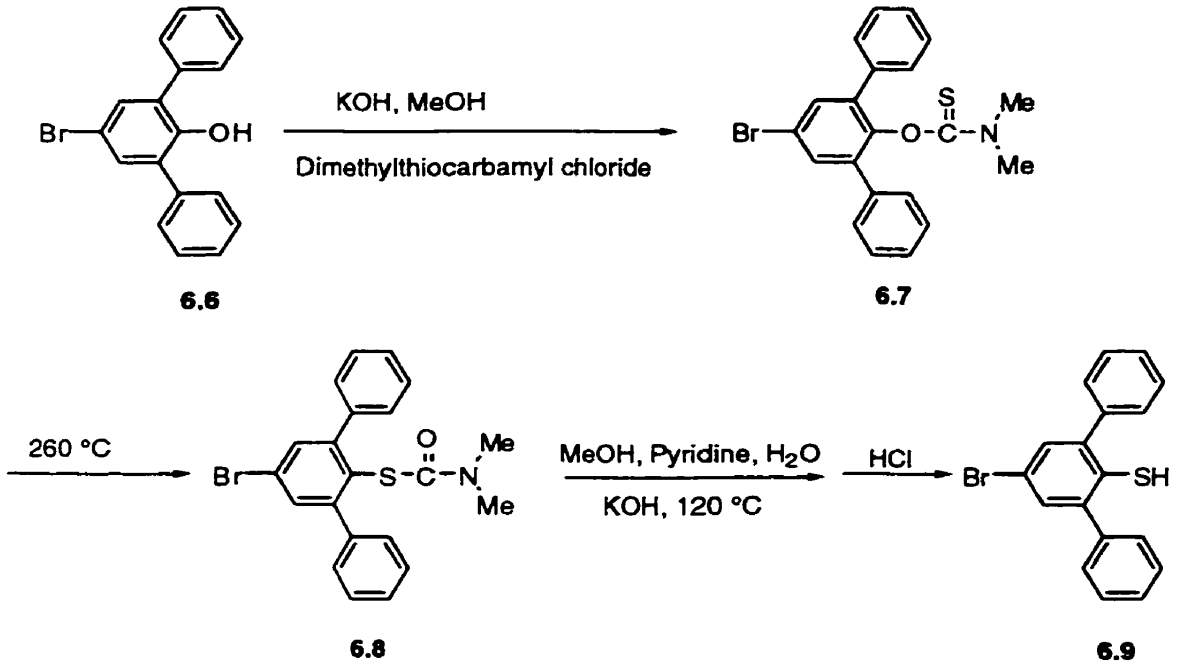


6.5

The synthesis of poly(2,6-diphenylphenylene ether) (**6.4**) was first reported in 1969.[28] This polymer has the advantage of high thermal stability, very low dielectric constant and very low moisture absorption.[29] However, this polymer has an extremely high melting point (501 °C) which precludes the possibility for melt processing. We

were interested in synthesizing the thioether anolog (**6.5**) of this polymer with the belief that the introducing of sulfur would lower the melting point.

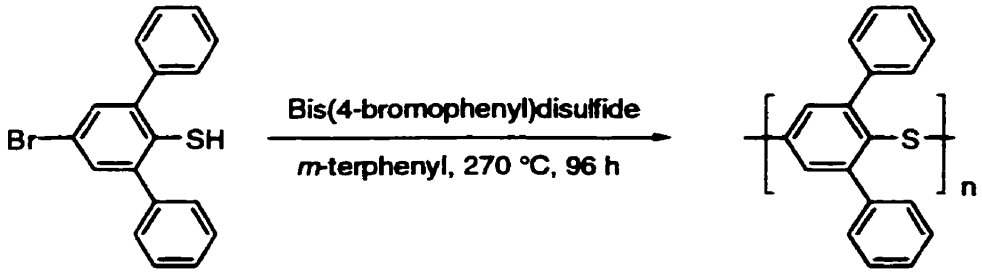
The synthesis of monomer 4-bromo-2,6-diphenylbenzenethiol is illustrated in Scheme 6.4. The 4-bromo-2,6-diphenylphenol was first transformed into the thiocarbamate (**6.7**) by treating **6.6** with ice-cold KOH methanolic solution and then adding dimethylthiocarbamyl chloride. The thiocarbamate was then heated at 260 ℃ without the presence of solvent for 2 h affording the desired rearranged product S-carbamate **6.8**. Hydrolysis of **6.8** with KOH in pyridine/methanol solution in the presence of small amount of water afforded the desired monomer 4-bromo-2,6-diphenylbenzenethiol after neutralization and recrystallization.



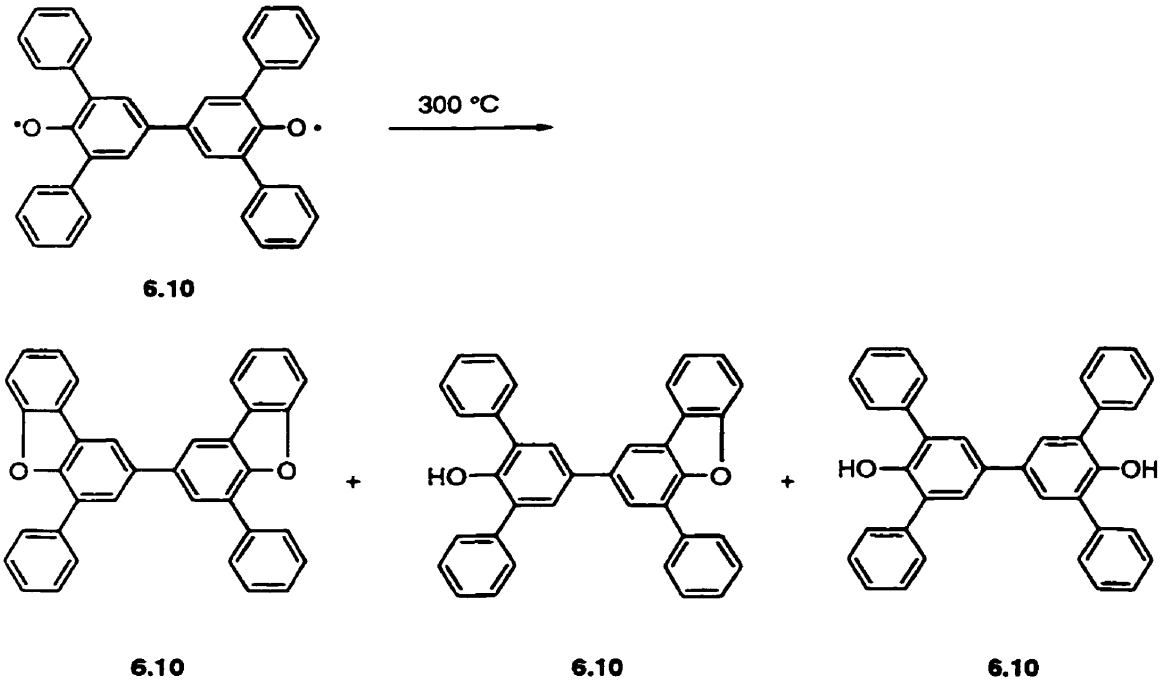
6.6 **6.7** **6.8** **6.9**

Scheme 6.4. Synthesis of 4-bromo-2,6-diphenylbenzenethiol

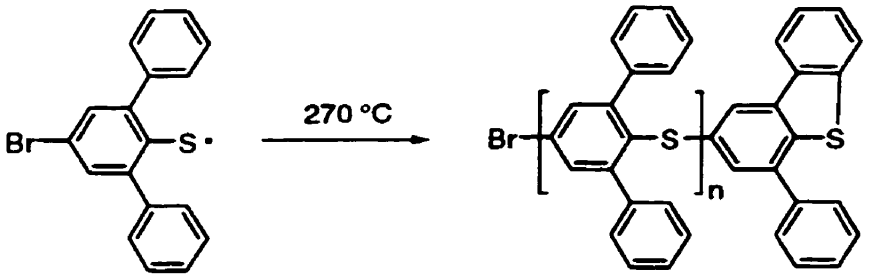
The attempted polymerization was carried as that for the polymerization of 4-bromobenzenethiol using 1 mol % of bis(4-bromophenyl)disulfide as the initiator (Scheme 6.5). However, only very low molecular weight oligomer was obtained after 96 h. GPC analysis indicated that the oligomer had a repeating uinit of 5 - 6. Hay found that tetraphenylbiphenoxide radicals form dibenzofuran derivatives at 300 ℃ (Scheme 6.6).[30] Here, we believe that the same type of reaction took place and hindered the formation of polymer (Scheme 6.7).



Scheme 6.5. Attempted polymerization of 4-bromo-2,6-diphenylbenzenethiol



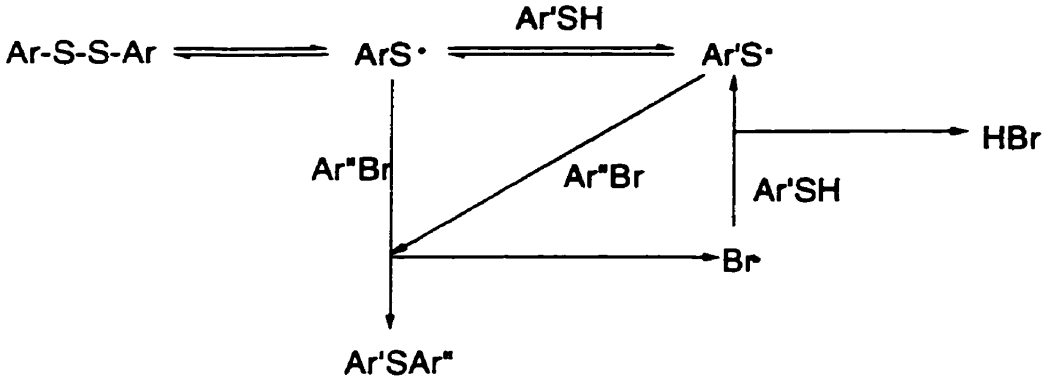
Scheme 6.6. Thermal reactions of a stable phenoxide radical



n = 0, 1,2,3,4, ...

Scheme 6.7. Possible chain termination mechanism for the free radical polymerization of 4-bromo-2,6-diphenylbenzenethiol

6.6. Polymerization mechanism.



Scheme 6.8. Proposed mechanism for polymerization between arylthiols and bromo compounds

One of the earliest methods used to prepare PPS was the polymerization of salts of 4-bromobenzenethiol.[23] This polymerization reaction has been described as a single-electron transfer process.[14,15] We have previously reported that bis(4-iodophenyl)disulfide on heating above 220 °C yields linear high molecular weight PPS along with elemental iodine.[11] This reaction is believed to operate by a free radical *ipso*-substitution mechanism.[11,31,32] When bis(4-bromophenyl)disulfide is heated, bromination of the solvent or oligomers occurs. Therefore, it is not suprising that the attempted polymerization of bis(4-bromophenyl)disulfide itself gave either no

polymerization[33] or very low molecular weight products.[11] However, high molecular weight polymers are formed if iodide ion is added to reduce the bromine radicals. By analogy, it appeares that bromine radicals generated from reaction of bis(4-bromophenyl)disulfide would react with the thiol group to generate HBr and thiyl radical. The chain reaction then continues and high molecular weight polymers are formed. The bromine radical plays a key role here (Scheme 6.8) by oxidation of the arylthiol to form a new thiyl radical with evolution of HBr.

6.7. Conclusions

A novel and feasible polymerization reaction, polymerization of 4-bromobenzenethiol, was demonstrated. The polymerization reaction was initiated by a free radical at 270 °C. High molecular weight PPS was obtained after 96 h reaction with the evolution of HBr as the sole side product. The reaction has also been extended to the polymerization of arylenedithiols with dibromoaromatic compounds. Attempted polymerization of 4-bromo-2,6-diphenylbenzenethiol failed to give high molecular weight polymer, presumably due to the formation of dibenzothiophene moieties which terminated the chain reaction.

6.8. Experimental section

Measurements.

DSC analyses were conducted on a Seiko 220 DSC instrument at a heating rate of 20 °C/min in nitrogen atmosphere (160 mL/min). Elemental analyses (C, H, S, and Br) were performed by Galbraith Laboratories, Inc. (Knoxville, TN). FT-IR spectra were measured with an Analect AQS-18 FTIR spectrometer and data was recorded with an Analect MAP-67 data system. High temperature GPC analyses were carried out on a Senshu Kagaku Model VHT-GPC SSC-7000 with a Soma Optics S-3750 UV/vis absorption detector set at 360 nm. Two Shodex AT80M/A columns and an AT-800P column from Showa Denko were installed. 1-Chloronaphthalene was used as the eluent and the flow rate was 1 mL/min. The temperatures of the column oven, the transfer line, and the flow cell were regulated at 210 °C. Polystyrene standards substituted by a fluorescent pyrene group were used as calibrating references.

Materials.

4-Bromobenzenethiol was purchased from Lancaster Synthesis Inc. and recrystallized from chloroform under N_2 atmosphere. *m*-Terphenyl, 1,4-dibromobenzene, sublimed sulfur, sublimed iodine, and bis(4-bromophenyl)ether were

purchased from Aldrich Chemical Inc. and used as received. 4,4'-Dibromobiphenyl, diphenyl disulfide, and 2,2'-dithiobis(benzothiazole) were obtained from commercial sources and were all recrystallized from absolute ethanol. Bis(4-bromophenyl)disulfide was prepared from benzenethiol and bromine.[34] Cyclic(arylene disulfide) oligomers **2.14a** were synthesized according to a previously reported method.[5] Compound **5.3h** was synthesized from bis(4-fluorobenzoyl)-3,4,5,6-tetraphenylbenzene as described previously.[13] 4-Bromo-2,6-diphenylphenol was prepared according to previously published procedures starting from 2,6-diphenylphenol.[35]

Synthesis of 4-bromo-(2,6-diphenyl)phenyl-O-thiocarbamate (6.7).

6.6 (16.3 g, 0.05 mol) was added to 100 mL of an ice cold KOH methanolic (3.1 g, 0.05 mol) solution and stirred at 0 °C for 0.5 h. N,N'-Dimethylthiocarbamoyl chloride (6.8 g, 0.06 mol) was then added in one portion and the mixture was stirred for another 10 h at room temperature. The precipitated white solid was collected by filtration and washed with ice-cold methanol : water (1 : 1) (150 mL). A white solid **6.7** (16.4 g, yield 79 %) was obtained after recrystallization from $CHCl_3$/methanol. M.p. 103 -104 °C. ^{1}H-NMR ($CDCl_3$): δ (ppm) 7.58 (s, 2H), 7.50 (d, 4H, J = 7.1 Hz), 7.43 (t, 4H, J = 7.1 Hz), 7.38 (m 2H), 3.03 (s, 3H), 2.93 (s, 3H). ^{13}C-NMR ($CDCl_3$): δ (ppm) 184.3, 146.9, 138.1, 136.0, 131.9, 129.1, 128.1, 127.9, 118.6, 42.4, 38.1. MS: *m/z* 412 (M^+, 16), 88(100), 72(83). HRMS: found, 411.0289; calcd for $C_{21}H_{18}BrNOS$, 411.0292.

Synthesis of 4-bromo-(2,6-diphenyl)phenyl-S-carbamate (6.8).

6.7 (15.0 g, 0.036 mol) was placed in a 100 mL of round-bottom flask and heated at 260 °C under N_2 atmosphere for 2 h. After recrystallization from absolute ethanol, a white solid **6.8** (11.8 g, yield 80 %) was obtained. M.p. 132 - 133 °C. ^{1}H-NMR ($CDCl_3$): δ (ppm) 7.53 (s, 2H), 7.35 (m, 10H), 2.66 (s, 6H). ^{13}C-NMR ($CDCl_3$): δ (ppm) 166.1, 150.1, 140.7, 132.5, 129.3, 127.5, 127.4, 126.0, 123.6, 36.9. MS: *m/z* 412(M^+, 26), 260(36), 72(100). HRMS: found, 411.0289; calcled for $C_{21}H_{18}BrNOS$, 411.0292.

Synthesis of 4-bromo-2,6-diphenylbenzenethiol (6.9).

6.8 (10.0 g, 0.024 mol), pyridine (30 mL), H_2O (6 mL), methanol (30 mL) and KOH (10.0 g, 0.18 mol) were charged in a flask and kept at reflux for 24 h under nitrogen atmosphere. The resulting mixture was cooled down, diluted with 250 mL of H_2O, and then acidified with conc. HCl. The oily precipitate was kept in a refrigerator overnight and it then solidified. The solid was filtered, washed with water and recrystallized with petrolum ether. A white crystalline product **6.9** was obtained. M.p. 51 - 52 °C. ^{1}H-NMR ($CDCl_3$): δ (ppm) 7.46 (t, 4H, J = 7.1 Hz), 7.41 (m, 6H), 7.36 (s, 2H), 3.39 (s, 1H, -SH). ^{13}C-NMR ($CDCl_3$): δ (ppm) 142.3, 140.1, 131.9, 129.1, 128.7, 128.2, 127.5, 118.0. MS: *m/z* 341(M^+,). MALDI-MS: found, 340; calcled for $C_{18}H_{13}BrS$, 340.

Polymerization of 4-bromobenzenethiol.

A typical example is given as follows. 4-Bromobenzenethiol (1.000 g, 5.29 mmol), bis(4-bromophenyl)disulfide (0.0199 g, 0.0529 mmol) and *m*-terphenyl (1.0 g) were charged in a Pyrex test tube (1.5 x 15 cm) and the test tube was placed in a salt bath preheated to 270 °C so that the contents were immersed to a depth of around 2 cm. The test tube was capped with a septum and a slow flow of nitrogen was passed through. Upon completion of the reaction (96 h), 3 mL of 1-chloronaphthalene was added to dilute the reaction mixture. The contents were poured into 200 mL of methanol to precipitate out the polymer. The methanol solution was heated to boiling and filtered. A white powder product (0.54 g, yield 95 %) was obtained after washing with 30 mL of hot $CHCl_3$, 30 mL of methanol, and drying at 100 °C in vacuo for 24 h.

Copolymerization of 4,4'-thio-bis(benzenethiol) with dibromo compounds.

A typical example is given as follows. 4,4'-Thio-bis(benzenethiol) (0.5 g, 2.0 mmol), 1,4-dibromobenzene (0.4710 g, 2.0 mmol), bis(4-bromophenyl)disulfide (0.0145 g, 0.04 mmol) and *m*-terphenyl (1.0 g) were charged in a Pyrex test tube (1.5 x 15 cm) and the test tube was placed in a salt bath preheated to 270 °C so that the contents were immersed to a depth of around 2 cm. The test tube was capped with a septum and a slow flow of nitrogen was passed through. Upon completion of the reaction (96 h), 3 mL of 1-chloronaphthalene was added to dilute the reaction mixture. The contents were poured into 200 mL of methanol to precipitate out the polymer. The methanol solution was heated to boiling and filtered. A white powder product (0.56 g,

yield 90 %) was obtained after washing with 30 mL of hot chloroform, 30 mL of methanol, and drying at 100 °C in vacuo for 24 h.

6.9. References and notes

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Chapter 7. Synthesis and Characterization of Amorphous Aromatic Poly(thioether ketone)s and Poly(thioether phenylphosphine oxide)s

7.1. Introduction

Due to their applications in the aerospace, electronic, automotive and related markets, high performance polymers are currently receiving considerable attention. Much research has been carried out in recent years toward the development of new or improved thermoplastic resins. In this area, aromatic poly(ether ketone)s have been given special attention because of their chemical resistance and excellent mechanical and thermal properties.

Only a few reports have been published on poly(thioether ketone)s, although conceptually their synthesis is similar to that of poly(ether ketone)s. In 1989, researchers at Dow Chemical reported the preparation of poly(thioether ketone)s from ketone activated aromatic fluoro compounds by reaction with anhydrous sodium sulfide in N-cyclohexyl-2-pyrrolidinone (CHP).[1] Senn studied the synthesis and characterization of *ran*-copoly(*p*-phenylene sulfide sulfone/ketone)s from sodium hydrosulfide[2]. Ueda *et al.* synthesized a series of poly(thioether ketone)s by the direct polycondensation of aromatic dicarboxylic acids with aryl compounds containing sulfide structures using phosphorous pentoxide / methanesulfonic acid (PPMA) as condensing agent and solvent[3]. Poly(thioether ketone)s have also been prepared from masked bisthiophenols in the presence of potassium bicarbonate.[4]

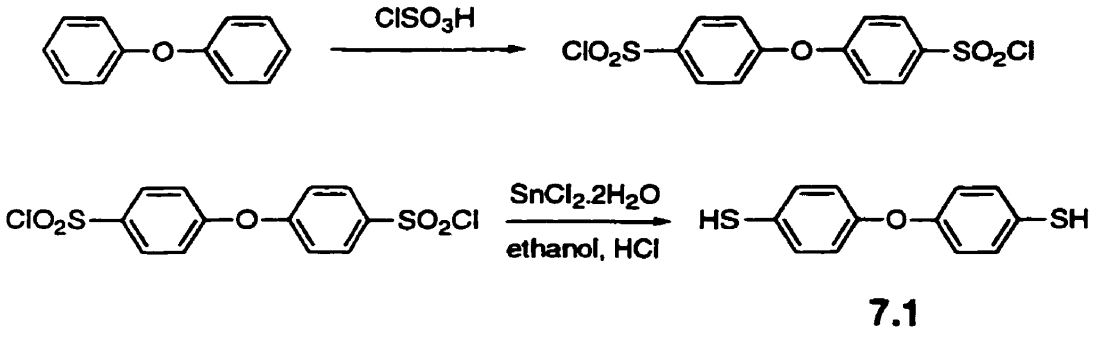
7.2. Strategy and goal

A major effort in our laboratory has been the synthesis of amorphous high performance materials. Over the years, a series of ketone containing monomers have been developed, and the properties of the poly(arylene ether ketone)s derived from them with a variety of bisphenols have been evaluated[5-7]. Most recently, a facile free-radical ring-opening polymerization of cyclic oligomers containing thioether linkages was developed in this laboratory[8], which greatly facilitated the processing of polymers. To broaden the research, more poly(thioether) polymers should be prepared and evaluated. Herein, we describe the synthesis and characterization of poly(thioether ketone)s prepared by reaction of ketone containing monomers with 4,4'-

oxybis(benzenethiol) and 4,4'-thiobis(benzenethiol). Poly(thioether phenyl phosphine oxide)s were also prepared from **7.1** and **7.2** by reaction with bis(4-fluorophenyl)phenylphosphine oxide (**7.4**). Poly(arylene ether)s from **7.4** have been extensively studied because of their high temperature stability, flame resistance, and resistance to oxygen plasma[9-11].

7.3. Monomer synthesis

The synthesis of monomer **7.1** is outlined in Scheme 7.1. Bis(4-chlorosulfonylphenyl)ether was selectively formed in the presence of excess of sulfonylchloride. The disulfonyl chloride was subjected to reduction with stannous chloride by Baron's modified method[12] and **7.1** was obtained in 73% yield.

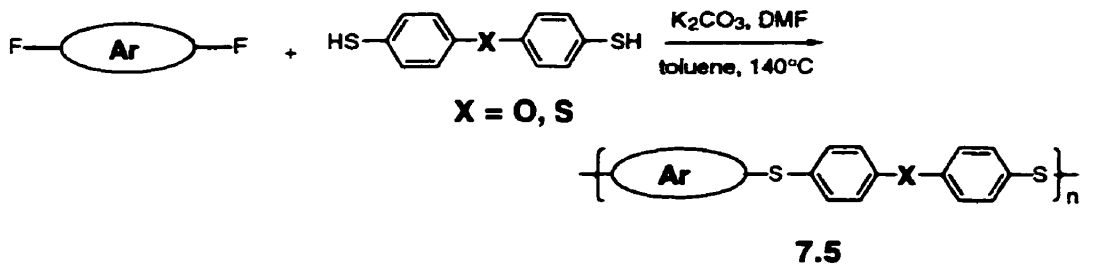


7.1

Scheme 7.1. Preparation of **7.1**

7.4. Polymer synthesis and characterization

The monomers **7.1** and **7.2** were polymerized with a series of ketone activated difluoro compounds **7.3a-e**, which were previously synthesized in this laboratory, and **7.4** in DMF (Scheme 7.2). This polymerization procedure was first described by Baron and Blank to synthesize poly(thioether sulfone) from bis(4-chlorophenyl)sulfone[12]. The thiophenoxide anions are stronger nucleophiles than phenoxide, therefore it is understandable that a lower temperature is necessary for the condensation reaction of thiophenoxide with fluoro compounds. High molecular weight poly(thioether ketone)s and poly(thioether phenyl phosphine oxide)s were generally obtained after 4 - 8 h of reaction times. All the polymers are amorphous and soluble in common organic solvents, such as chloroform, toluene, DMF, DMAc and NMP.



7.5

F—Ar—F	X	7.5	F—Ar—F	X	7.5
7.3a	O	7.5a	7.3d	O	7.5g
	S	7.5b		S	7.5h
7.3b	O	7.5c	7.3e	O	7.5i
	S	7.5d		S	7.5j
7.3c	O	7.5e	7.4	O	7.5k
	S	7.5f		S	7.5l

Scheme 7.2. Synthesis of novel poly(arylene thioether)s

The polymers were characterized by ^{1}H-NMR. The 1D ^{1}H-NMR and 2D COSY spectra in $CDCl_3$ of polymer **7.5f** are shown in Figure 1a and 1b, respectively. The H_1 signal shifted to 7.47 ppm from 7.60 ppm[5] following polymerization due to the replacement of fluoro atoms by sulfur atom, while the H_2 signal shifted downfield from ~6.9 ppm to 7.01 ppm.

The apparent molecular weights of the polymers were obtained by GPC and are given in Table 7.1. Polymers **7.5k** and **7.5l** appear to interact with the column using chloroform as eluent, and hence their apparent molecular weights are not available. The monomer **7.3a** gave rise to polymers with very broad distribution as suggested by GPC results. This indicates that some cross-linking or branching reaction occurred during the polymerization process. The formation of narrow distribution polymers **7.5g** and **7.5h** shows that the four fluorine atoms on the four pendant phenyl rings

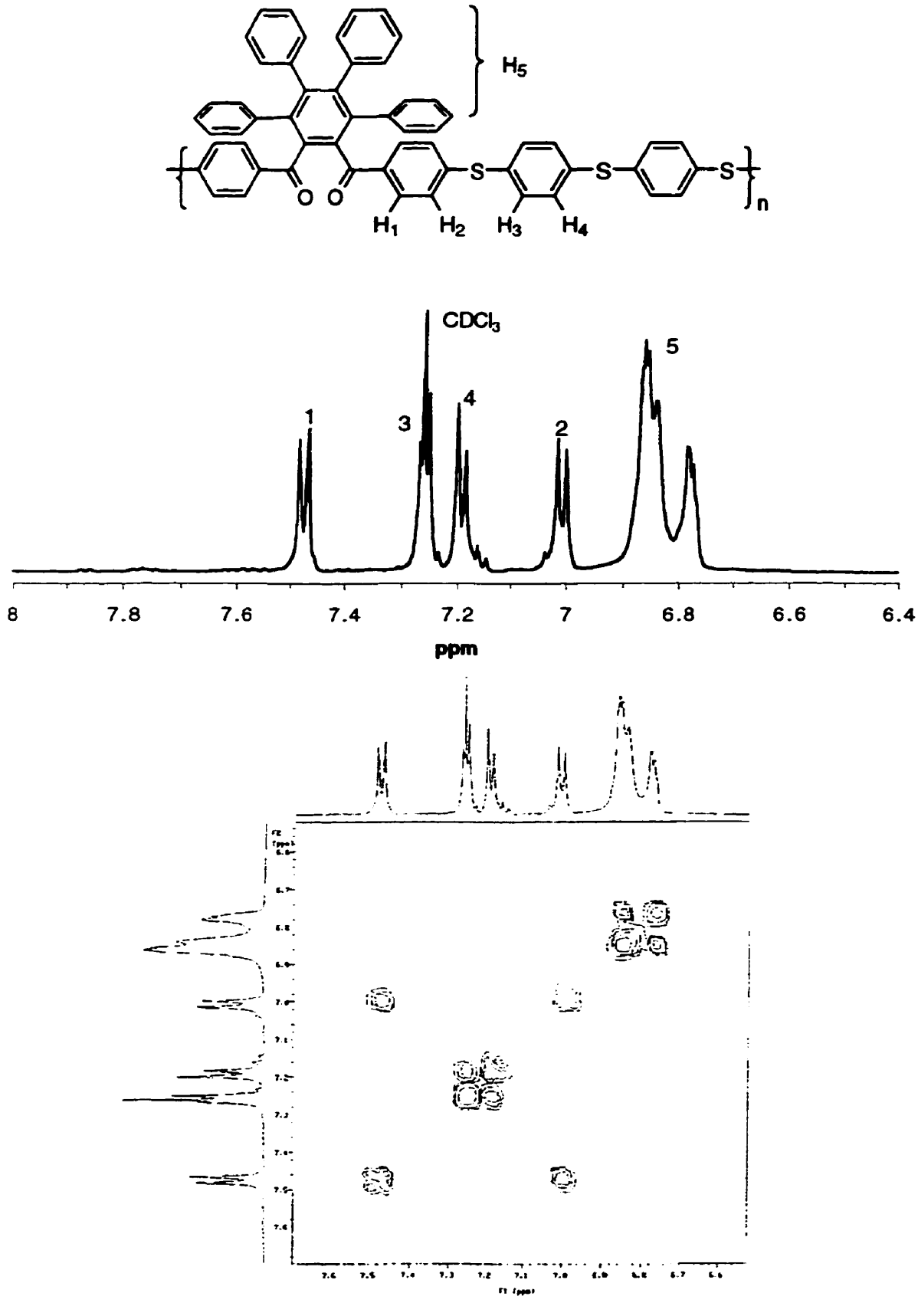


Figure 7.1. NMR spectra of polymer **7.5f**

were not replaced by a sulfur atom. As indicated by ^{19}F-NMR and HMO calculations, the ketone activated fluoro atom has considerably higher reactivity than a fluoro atom without activation, however suitable low temperature conditions have to be maintained to avoid branching[6].

Table 7.1. GPC data for polymers **7.5a-j**

Polymer	Mn (g/mol)	Mw (g/mol)	Polydispersity
7.5a	68,000	534,000	7.9
7.5b	55,000	801,000	14.6
7.5c	68,000	156,000	2.3
7.5d	90,000	155,000	1.7
7.5e	69,000	107,000	1.6
7.5f	62,000	102,000	1.6
7.5g	88,000	124,000	1.4
7.5h	92,000	126,000	1.4
7.5i	100,000	162,000	1.6
7.5j	65,000	102,000	1.6

Inherent viscosities were taken at a concentration of 0.5 g/dL in chloroform solution and the results are listed in Table 7.2. The inherent viscosities of these polymers vary from 0.30 to 0.88.

The glass transition temperatures (T_gs) of polymers **7.5** were measured by differential scanning calorimetry at a heating rate of 20 °C/min under an atmosphere of nitrogen (Table 7.2). The T_gs of these polymers range from 154-251 °C. As observed previously[5], the increasing number of pendant phenyl groups going from monomer **7.3a** to monomer **7.3c** resulted in the T_gs of the resultant polymers increasing from around 150 to 230 °C. Changing the **X** group of the dithiol compounds from oxygen to sulfur led to a decrease in the T_gs. For example, the polymers **7.5e** and **7.5k** have T_gs of 237 and 195 °C respectively, however, their sulfur counterparts **7.5f** and **7.5l**

have lower T_gs of 227 and 182 °C. This is understandable since the C-S bond is more flexible than the C-O bond. In terms of glass transition temperature, monomer **7.4** is equivalent to monomer **7.3b**.

Table 7.2. Properties of polymers **7.5a-l**

			TGA (°C)[c] (5% Wt Loss)	
Polymer	Inherent viscosity[a]	T_g (°C)[b]	N_2	Air
7.5a	0.88	161	462	503
7.5b	0.40	154	420	502
7.5c	0.50	203	496	510
7.5d	0.43	192	499	522
7.5e	0.30	237	517	518
7.5f	0.36	227	537	527
7.5g	0.46	228	541	520
7.5h	0.35	232	520	518
7.5i	0.42	251	515	527
7.5j	0.31	225	514	514
7.5k	0.37	195	511	508
7.5l	0.32	182	506	503

a. 0.5 g/dL in chloroform at 25 °C.

b. Heating rate was 20 °C/min under nitrogen atmosphere.

c. Heating rate was 20 °C/min

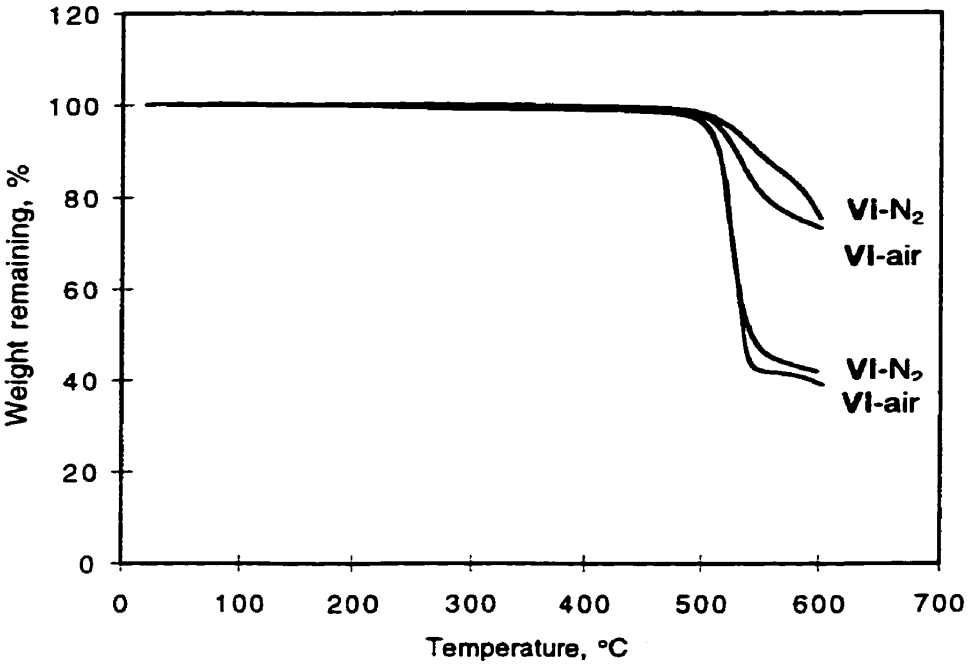


Figure 7.2. TGA curves of polymers **7.5i** and **7.5l** in nitrogen and air atmospheres

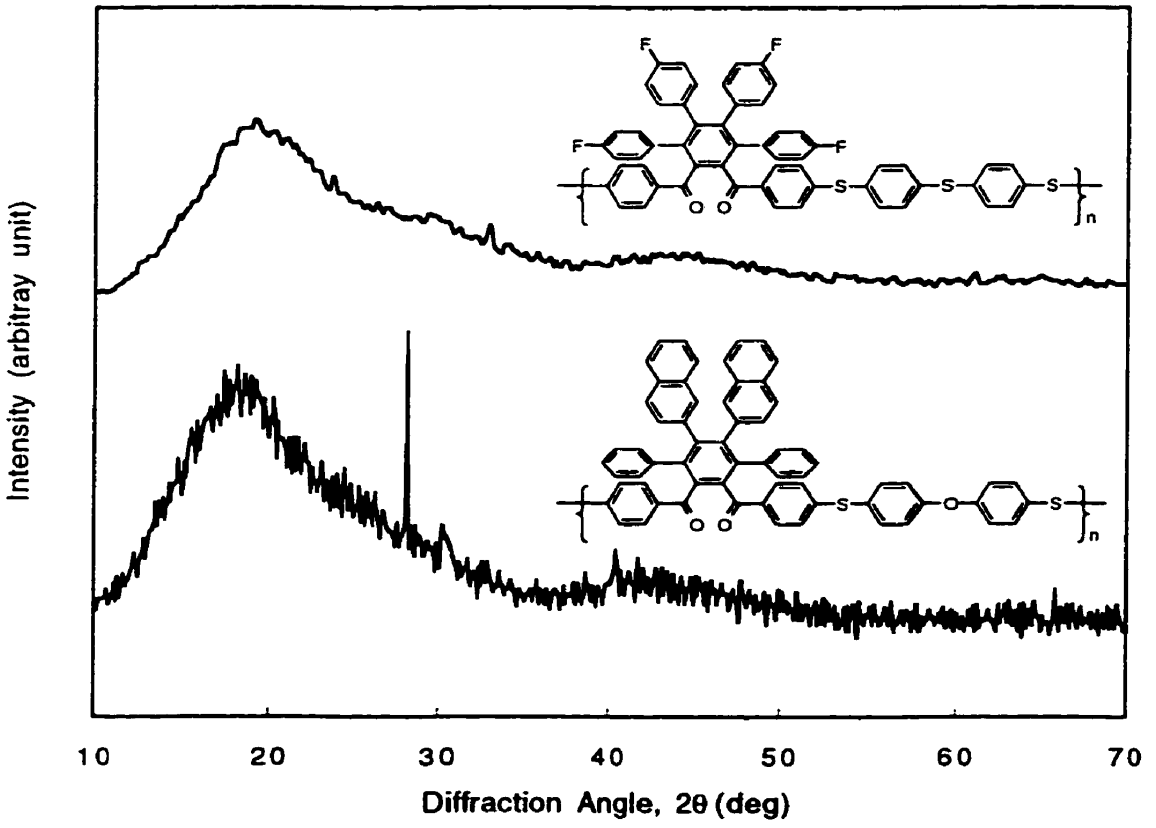


Figure 7.3. WAXD curves of polymer **7.5h** and **7.5i**

All polymers showed excellent stability according to their thermogravimetric analysis in nitrogen and air atmospheres (Table 7.2). Polymer **7.5b** showed the poorest thermal stability in a nitrogen atmosphere based on the 5% weight loss temperature. The 5% weight losses are above 500 °C for all the polymers tested under air atmosphere and generally they are higher than that obtained under nitrogen atmosphere. We speculate this is because sulfur tends to be oxidized at high temperatures and gains some weight. This apparent thermal stability which is higher in air than in nitrogen has also been noticed by other researchers in other polymer systems[13]. It is interesting to note that again polymers **7.5c** and **7.5d** showed almost the same thermal stabilities as those of polymers prepared from monomer **7.4**, although polymers **7.5k** and **7.5l** had a slightly lower thermal stabilty in air than that in nitrogen. In terms of char weight remaining after 500 °C, polymers **7.5a-l** were more stable in nitrogen atmosphere than in air atmosphere. TGA charts in Figure 7.2 indicate that the weight losses of polymers **7.5i** and **7.5l** were faster in the air than in nitrogen above the 5% weight loss temperatures.

Wide-angle x-ray diffraction (WAXD) measurements were made for the film samples of polymer **7.5h** and **7.5i** (Figure 7.3). The WAXD curves indicated the polymers to be amorphous. It is well known that poly(*p*-phenylene sulfide) (PPS) is a highly crystalline polymer. The WAXD result showed that a PPS chain with three repeating units is not sufficient to form any crystallinity.

7.5. Conclusions

A series of poly(thioether ketone)s and poly(thioether phenylphosphine oxide)s were successfully prepared from dithiol compounds **7.1** and **7.2** by reaction with a series of ketone activated aromatic difluoro compounds **7.3a-e** and **7.4** in DMF in the presence of anhydrous potassium carbonate. The polymers formed were amorphous as evidenced by WAXD measurements, and soluble in normal organic solvents. They had inherent viscosities of 0.3-0.88 g/dL in chloroform at 25 °C. The glass transition temperatures of these polythioethers were in the range of 154-251 °C. The 5% weight loss temperatures by TGA were in the range of 420-541 °C in N_2 and 503-527 °C in air.

7.6. Experimental section

Materials

The required 4,4'-thiobis(benzenethiol) was purchased from Aldrich Chemical Inc. and recrystallized from absolute ethanol. **7.3a**, **7.3b**, and **7.3c** were prepared

according to previously published method[5]. The synthesis of **7.3d** and **7.3e** have been published elsewhere[6,7]. **7.4** was synthesized by a Grignard technique[10]. DMF was purchased from Aldrich Chemical Inc. and used directly without further purification.

Synthesis of bis(4-chlorosulfonylphenyl)ether

A three-neck round bottom flask was charged with 100 mL of chlorosulfonic acid and cooled to 0 °C. To this cooled solution, 40.0 g (0.235 mol) of diphenyl ether was added dropwise over a 3 h period through a dropping funnel and the resulting mixture was allowed to stir at room temperature for another 8 h. The mixture was then carefully poured into 1 kg of ice and the resulting white solid was filtered. Recrystallization from hexane yielded 61.6 g of the desired product. m.p. 126-127 °C (lit.[14] 128-129 °C)

Synthesis of 4,4'-oxybis(benzenethiol)[12]

A 1000 mL three-neck round bottom flask equipped with a magnetic stirrer, a thermometer, and a reflux condenser was charged with 38.0 g of bis(4-chlorosulfonylphenyl)ether (0.104 mol), 250 g (1.1 mol) of stannous chloride dihydrate, and 300 mL each of anhydrous ethanol and concentrated hydrochloric acid. The mixture was heated to reflux for 8 h, cooled to room temperature, poured into 500 mL of concentrated hydrochloric acid and filtered. The crude product was dissolved in 500 mL of 5% NaOH and precipitated out by adding concentrated hydrochloric acid to the filtrate. **7.1** (17.7 g) was obtained by recrystallization from ethanol. Yield, 73%. m.p.: 103-104 °C (Lit.[15] 103-104 °C).

Polymerization

Polymerization reactions were conducted in a 50 mL three neck flask equipped with a gas inlet, a thermometer, a Dean-Stark trap, and reflux condenser. A typical example is given below. A flask was charged with 1.2520 g (2.0 mmol) of **7.3c**, 0.5008 g (2.0 mmol) of **7.2**, 0.54 g (3.9 mmol) anhydrous K_2CO_3, 6.0 mL of DMF and 5 mL of toluene. The reaction mixture was blanketted with nitrogen and placed in a preheated oil bath. Toluene was gradually removed and the temperature of the reaction mixture was raised to 140-145 °C and kept at that temperature until the viscosity increased dramatically. The reaction mixture was cooled and diluted with 8 mL DMF, and several drops of acetic acid were added to neutralize the thiophenoxide

end groups. The polymer solution was then poured into vigorously stirred methanol (100 mL) and filtered, redissolved in chloroform, and filtered through a thin layer of Celite. The chloroform solution was concentrated and then coagulated in methanol. The fibrous polymer was recovered by filtration and dried under vacuum at 120 °C for 24 h.

Characterization

^{1}H-NMR spectra were recorded on a Varian UNITY-500 spectrometer using chloroform-*d* as solvent. Gel permeation chromatography (GPC) was performed on a Waters 510 HPLC equipped with 5μ phenogel columns (linear, 3 x 500 Å) arranged in series and a UV detector at 254 nm. Chloroform was used as eluent with polystyrene standards. Glass transition temperatures were determined on a Seiko 220 DSC instrument at a heating rate of 20 °C/min under a nitrogen atmosphere. Thermogravimetric analysis (TGA) data were obtained using a Seiko TG/DTA instrument at a heating rate of 20 °C/min in nitrogen or air atmosphere. Inherent viscosities were measured using chloroform solution at a concentration of 0.5 g/dL in a Ubbelohde viscometer. WAXD measurements were performed on a Philips PW1710 based X-ray diffractometer using CuK α radiation with the films cast from chloroform solution. The intensity of one second counts was taken every 0.02 degrees (2Θ).

7.7. References and notes

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Chapter 8. Novel Synthesis of Poly(arylene thioether)s *via* One-pot Polymerization of Bis(N,N'-dimethyl-S-carbamate)s with Activated Dihalo Aromatic Compounds

8.1. Introduction

Poly(phenylene sulfide) (PPS) and poly(ether sulfone)s are very important commercial high performance polymers. The incorporation of thioether linkages into the polymers provides the excellent properties associated with PPS into the polymers, such as excellent nonflammability, low moisture absorption, high dimensional stability, and good compatibility with inorganic fillers. However, research on the synthesis and study of poly(arylene thioether)s is very limited, compared with their counterparts the poly(arylene ether)s. One of the most commonly used methods to prepare poly(arylene ether)s is the reaction of dihydroxy aromatic compounds with activated dihalo compounds in the presence of potassium carbonate as a base in a polar solvent, such as N,N-dimethylacetamide (DMAc) or N-methylpyrrolidinone (NMP).[1] Several dihydroxy compounds are readily available commercially, however, the availability of arylene dithiols is very limited because of their instability and unpleasant odor.

Several reports have appeared in the literature for the preparation of poly(arylene thioether)s. From a few arylene dithiols, a series of poly(arylene thioether ketone)s[2] and poly(arylene thioether sulfone)s[3] were synthesized in N,N-dimethylformamide (DMF) in the presence of anhydrous K_2CO_3. Poly(thioether ketone)s and poly(thioether)s were also prepared from activated aromatic fluoro compounds and anhydrous sodium sulfide in N-cyclohexyl-2-pyrrolidinone (CHP)[4] or with sodium hydrosulfide.[5] By using phosphorous pentoxide/methanesulfonic acid (PPMA) as condensing agent and solvent, Ueda *et al* synthesized a series of poly(thioether ketone)s.[6] Silylated dithiols[7] and S-(N-propyl carbamate) masked dithiols[8] have been prepared and used to prepare poly(arylene thioether)s. However, they are either moisture sensitve and unreactive or have to be prepared from existing dithiol compounds, which limits their availability. We have also prepared many poly(thioether)s from cyclic(arylene disulfide) oligomers and iodo or bromo compounds[9,10] as well as from the polymerization of arylenedithiols with dibromo

compounds in the presence of a free radical initiator,[11,12] as described in previous chapters.

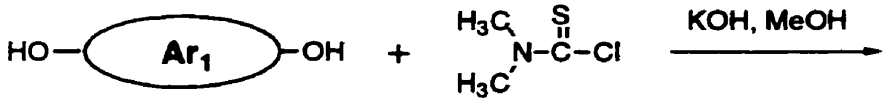
8.2. Strategy and goals

An elegant synthesis of arylthiols is the Newman-Kwart rearrangement reaction.[13] By using this reaction, many N,N'-dimethyl-S-carbamate masked arylene dithiols can be conveniently prepared from the readily available dihydroxy aromatic compounds. If the one-pot polymerization of N,N'-dimethyl-S-carbamate masked arylene dithiols and activated dihalo aromatic compounds is successful, a wide variety of poly(arylene thioether)s would be readily available from easily availabe dihydroxy compounds and the isolation and purification of the thiols would be avoided. Since thioethers can also be readily oxidized to form sulfones, many poly(arylene sulfone)s would also become readily available. In this chapter, we will describe our success in the preparation of poly(arylene thioether)s by a one-pot polymerization of N,N'-dimethyl-S-carbamate masked dithiols and activated dihalo aromatic compounds. A series of novel poly(arylene thioether)s were prepared and characterized.

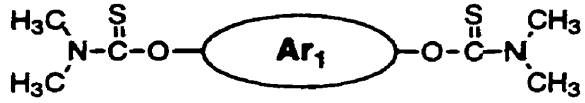
8.3. Monomer synthesis

Our objective was to establish a convenient and general method for the preparation of a series of novel poly(arylene thioether) polymers. Two commonly used dihydroxy compounds, 9,9'-bis(4-hydroxyphenyl)fluorene and 2,2'-bis(4-hydroxyphenyl)hexafluoropropane, as well as a potentially inexpensive and easily prepared heterocyclic monomer, 1,2-dihydro-4-(4-hydroxyphenyl)(2*H*)phthalazin-1-one (**8.5**),[14,15] were used to demonstrate the synthetic method. Fluorene containing polymers have high glass transition temperatures, high thermal stabilities, and good solubilities.[16] The incorporation of the hexafluoroisopropylidene group into polymers increases the solubility, thermal stability, flame resistance, oxidation resistance, adhension and optical transparency while decreasing the crystallinity, dielectric constant and water absorption of polymers.[17] The monomer (**8.5**) forms high temperature polymers with excellent thermal and hydrolytic stability by polymerization with activated dihalo compounds. The polymerization reaction has been confirmed to proceed *via* a novel N-C coupling reaction by spectroscopic studies.[18] A series of new monomers have been synthesized and polymerized to form high temperature polymers by taking advantage of this novel polymerization reaction.[19] There are two kinds of active hydrogens in **8.5**, an active O-H and an active N-H. Experimently, we

have found that the acidity of the O-H group is higher than that of the N-H group and we have been able to selectively convert the O-H group into the S-(N,N'-dimethyl carbamate) group to give the novel monomer **8.7**.



8.1



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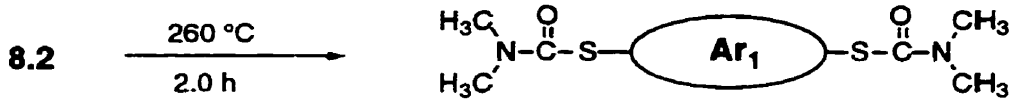

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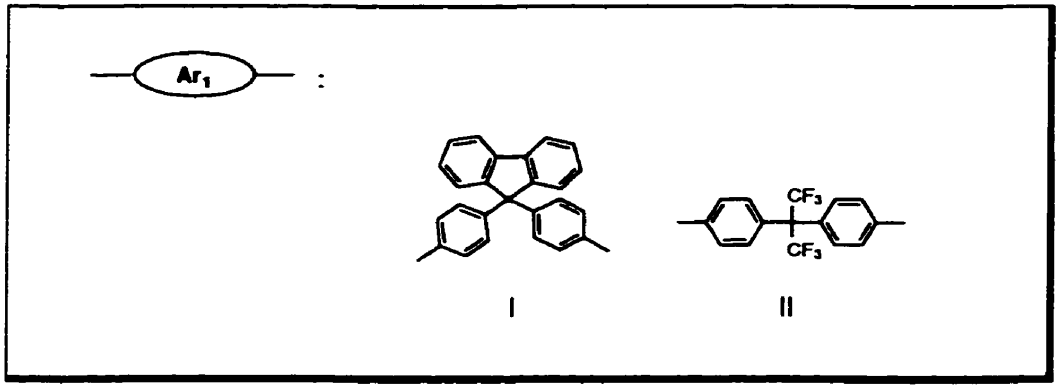
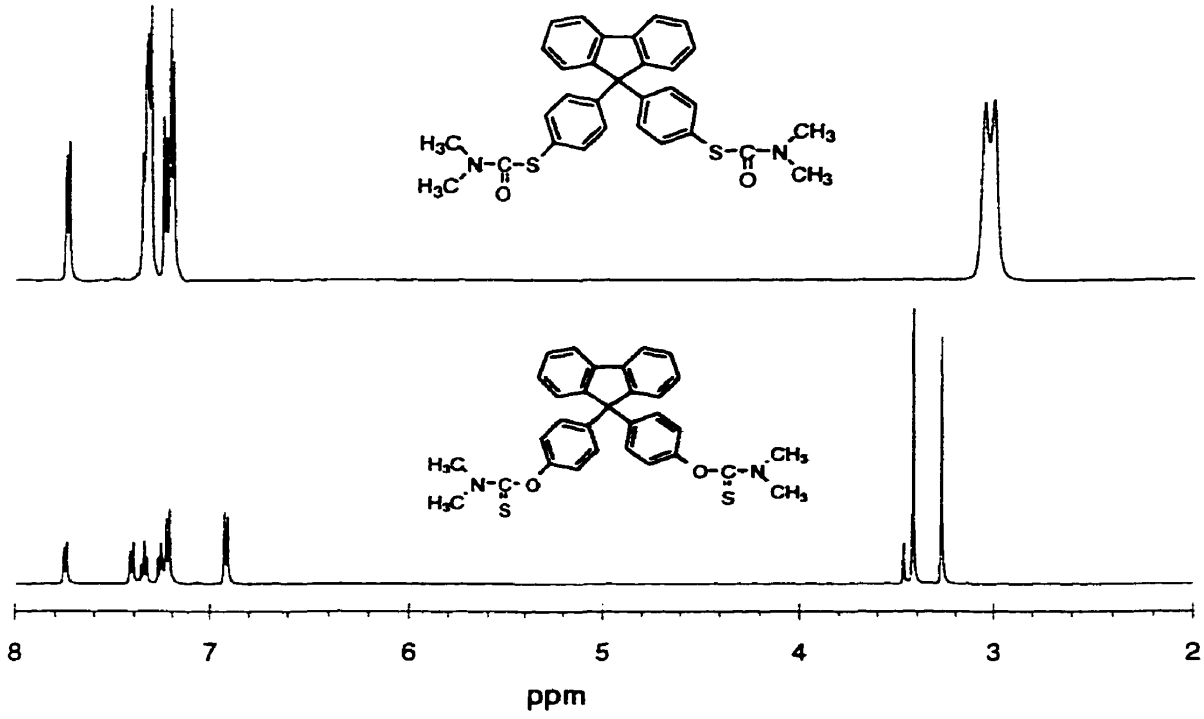


Scheme 8.1. Syntheses of N,N'-dimethyl-S-carbamate masked arylene dithiols



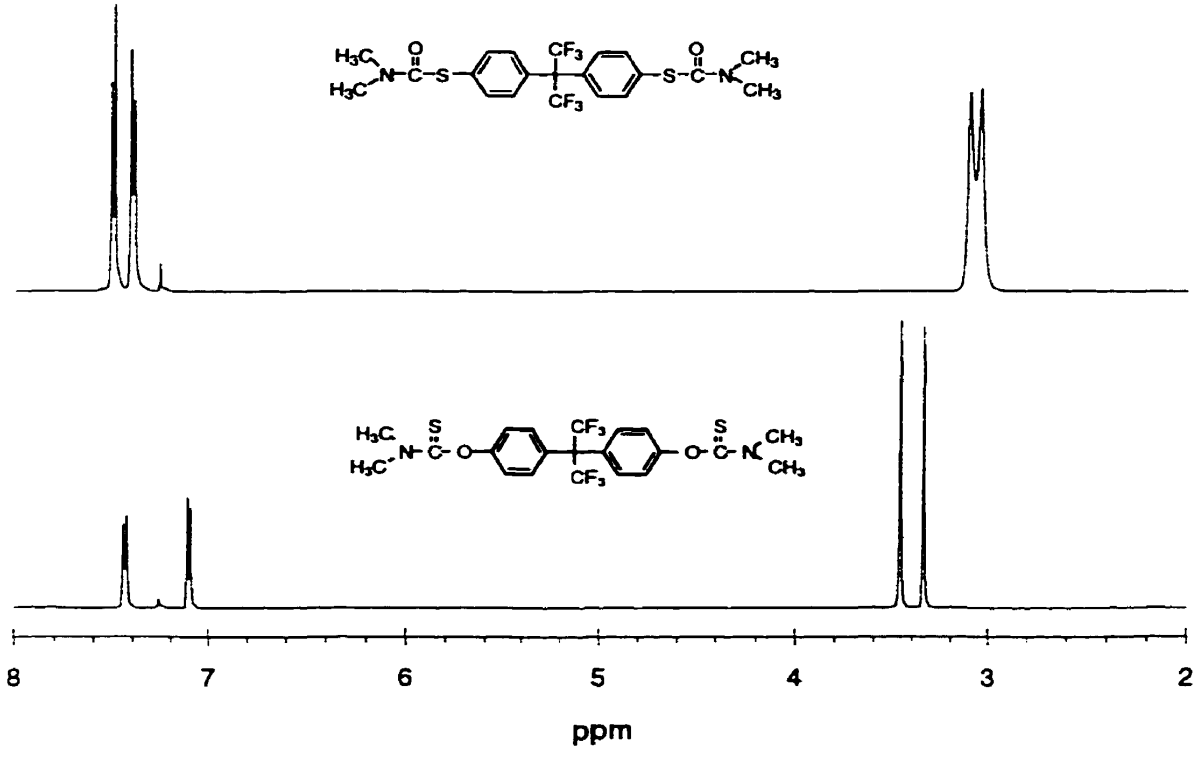
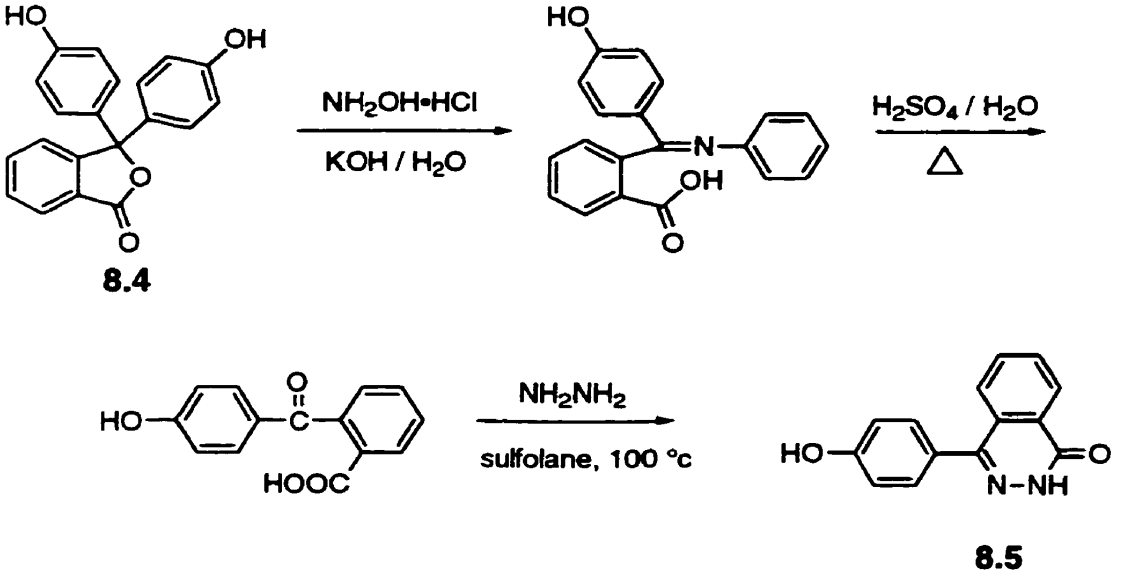


Figure 8.1. ^{1}H-NMR spectra of O-(N,N'-dimethyl thiocarbamate)s **8.2** and S-(N,N'-dimethyl carbamate)s **8.3** ($CDCl_3$)

The synthesis of the N,N'-dimethyl-S-carbamate masked dithiols is very straightforward and is illustrated in Scheme 8.1. The N,N'-dimethyl-O-thiocarbamates were prepared from the respective dihydroxy compounds in chilled methanolic KOH solution. The rearrangement reactions were readily carried out at 260 °C. Diphenyl ether was used as solvent for the rearrangement of the fluorene containing thiocarbamate. However, no solvent was necessary for the rearrangement of the hexafluoroisopropylidene containing thiocarbamate. The rearrangement reactions have been confirmed by HPLC and ^{1}H-NMR. The retention times were longer for **8.3I-II** than those of **8.2I-II** in HPLC using methanol as the eluent. The comparison of ^{1}H-NMR spectra of **8.2I-II** and **8.3I-II** are shown in Figure 8.1. The two sets of well separated doublets from the benzene rings substituted by N,N'-dimethyl-O-thiocarbamate moved closer and down field after rearrangement to the N,N'-dimethyl-S-carbamates for both **I** and **II**. The proton signals of the dimethyl groups in N,N'-dimethyl-O-thiocarbamate groups are at lower fields and sharper than those of the N,N'-dimethyl-S-carbamates.



Scheme 8.2. Synthesis of phthalazinone monomer **8.5**

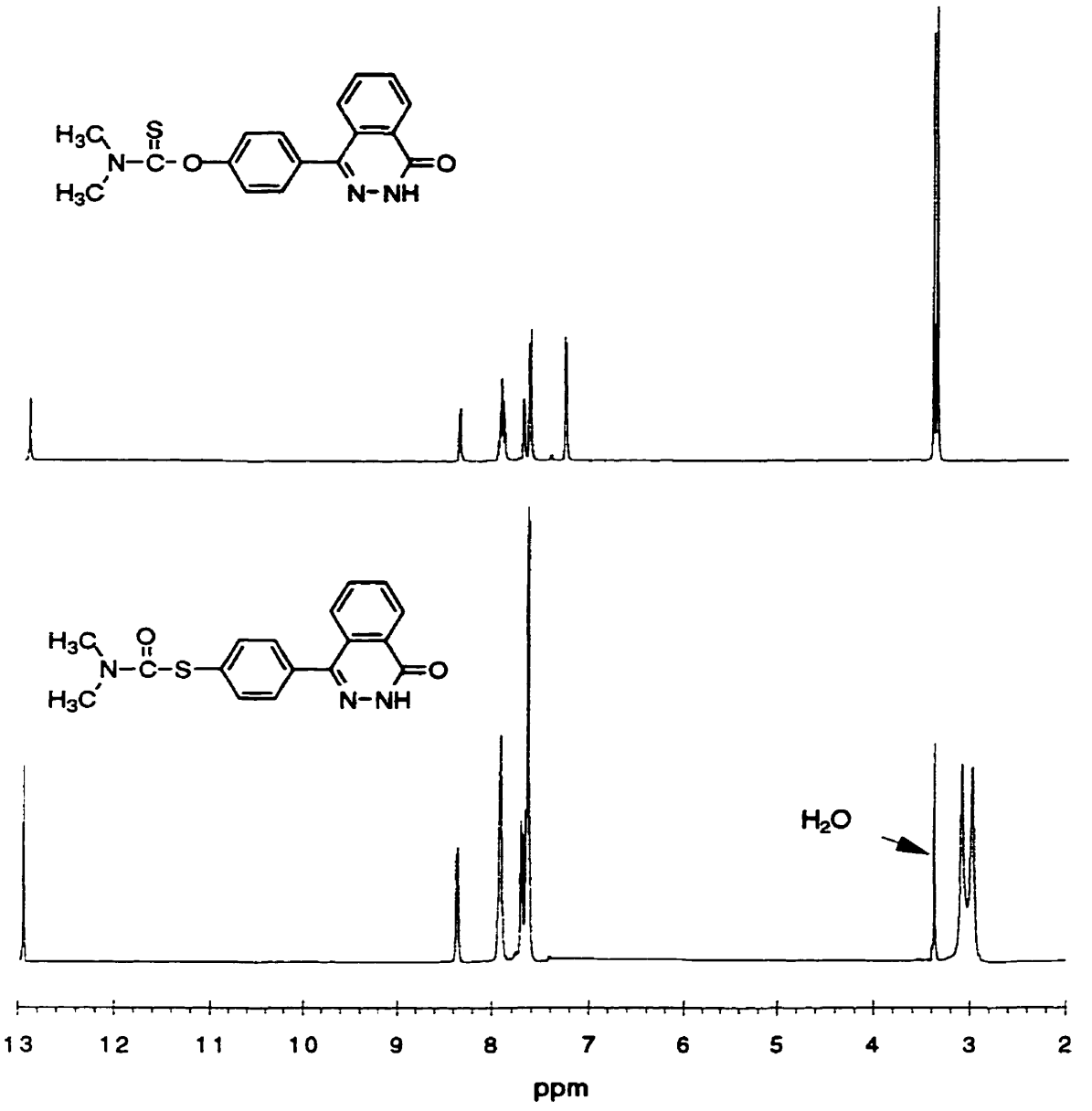
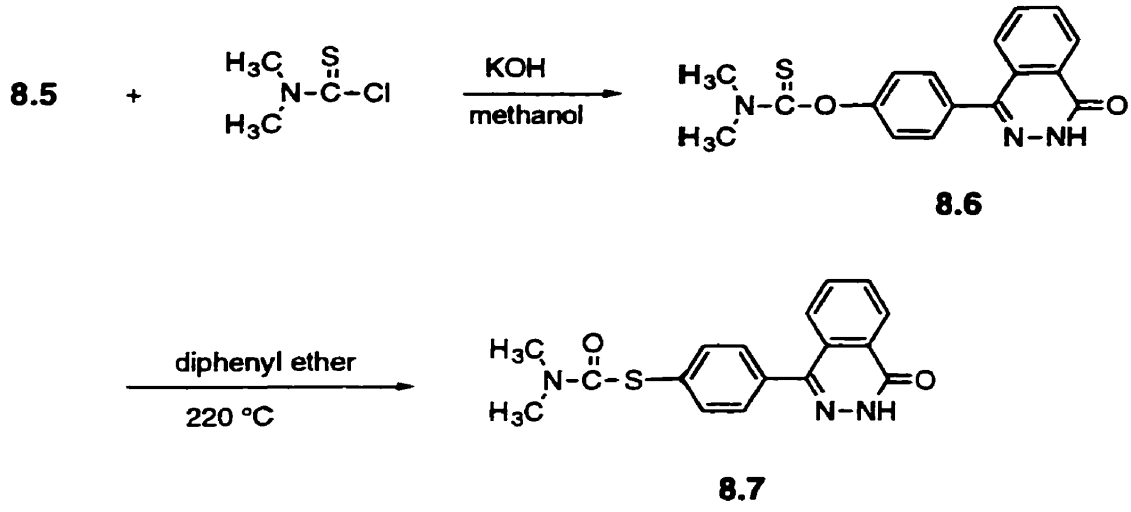


Figure 8.2. ^{1}H-NMR spectra of monomer **8.6** and **8.7**

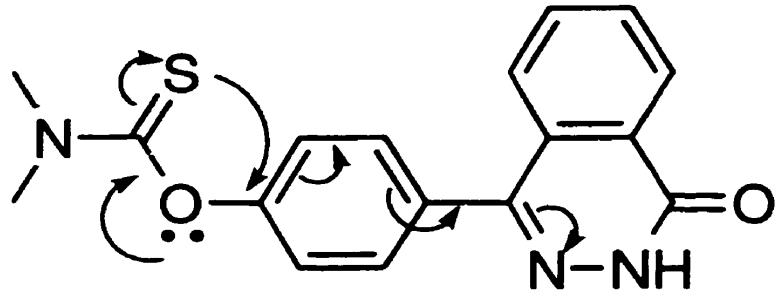
The synthesis of monomer **8.5** was first described in 1993,[14] starting from phenolphthalein (**8.4**) in three steps (Scheme 8.2). The full characterization of this monomer has been published.[15,18] The NMR proton signals of the O-H and N-H groups for **8.5** are at $\delta = 9.81$ ppm and 12.74 ppm, respectively.[18] By reacting with one equivalent of potassium hydroxide in ice-chilled methanol solution, the hydroxy group in **8.5** was selectively transformed into the N,N'-dimethylthiocarbamate group to give **8.6**. The selectivity has been confirmed by ^{1}H-NMR studies. In the ^{1}H-NMR spectrum of **8.6** taken in DMSO-*d* 6 solvent, the proton signal corresponding to the O-H has disappeared due to the formation of the N,N'-dimethylthiocarbamate group, while the proton signal corresponding to N-H ($\delta = 12.9$ ppm) is still remaining.



Scheme 8.3. Synthesis of the S-(N,N'-dimethylcarbamate) monomer **8.7**

The synthesis of **8.7** was realized by the Newman-Kwart rearrangement reaction. The reaction was carried out at 220 °C in an inert solvent, diphenyl ether, which was used to keep the reactants in the solution at the reaction temperature. The reaction proceeds through a four member ring intermediate which is stabilized by electron withdrawing groups. Due to the electron withdrawing property of the heterocyclic ring (Scheme 8.4), the rearrangement reaction from **8.6** to **8.7** readily took place at a lower temperature than that required for monomers without electron withdrawing groups. The completion of the rearrangement reaction was confirmed by HPLC and NMR studies. **8.7** has a longer retention time than that of **8.6**. The

conversion of the reaction was 98 % as determined by HPLC. The comparison of ^{1}H-NMR spectra of **8.6** and **8.7** are shown in Figure 8.2. The methyl groups in **8.7** are at lower field and much broader than those in **8.6**. Another characteristic change is that the two sets of doublets of the benzene ring adjacent to the carbamate group in **8.7** are much closer that those of **8.6**.

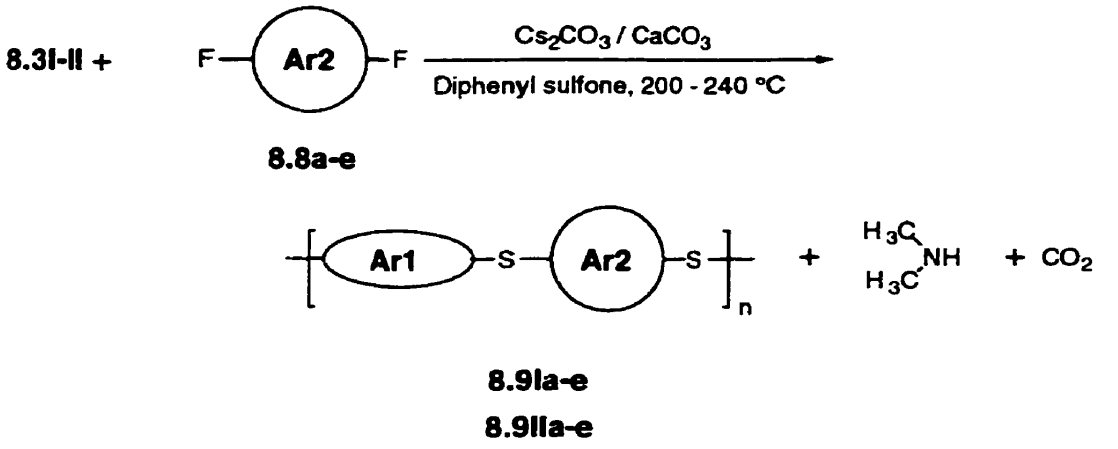


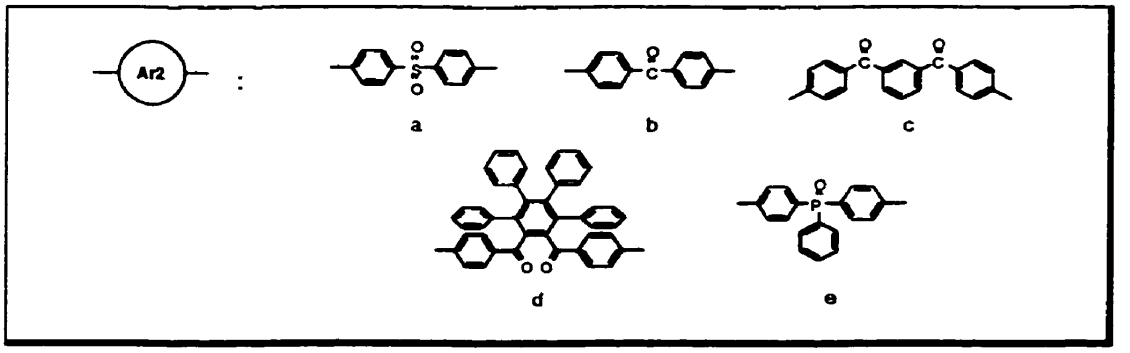
Scheme 8.4. Mechanism for the Newman-Kwart rearrangement reaction

8.4. Polymer synthesis

The one-pot polymerization of N,N'-dimethyl-S-carbamate masked dithiols and activated dihalo aromatic compounds is shown in Scheme 8.5. It has been shown that N,N'-dimethyl carbamates can not be cleaved by K_2CO_3 in NMP at reflux temperature over a 24 hour period, although the same system has been successfully used to prepare polymers from N-propyl carbamate masked phenols or thiophenols.[8,20] This is due to the active N-H bond in the N-propyl carbamate which facilities the cleavage.[21] We have now found that N,N'-dimethyl-S-carbamate masked arylene dithiols can be efficiently cleaved with the formation of N,N-dimethylamine and CO_2 at 200 - 240 °C in diphenyl sulfone in the presence of a cesium carbonate and calcium carbonate mixture. High molecular weight polymers can be readily prepared within 3 - 4 hours in a one-pot reaction between bis(N,N'-dimethyl-S-carbamate)s and activated dihalo aromatic compounds. Generally, after 2 hours of reaction, the reaction mixture became very viscous and additional diphenyl sulfone had to be added to dilute the mixture. DMAc and NMP, which are commonly used for polymerization reactions which proceed *via* a nucleophilic substitution reaction, are not suitable for the present polymerization reaction. The active methyl or methylene groups interfere with the polymerization reactions and high molecular weight polymers could not be obtained. To obtain high molecular weight polymers, it is also necessary to carry out the

polymerization at relatively lower temperatures at the beginning, and then gradually increase the temperature. When the polymerization reactions were started at higher temperatures (> 250 °C), only low molecular weight oligomers were obtained. Fukawa and Tanabe have observed that 4,4'-difluorobenzophenone reacts with potassium carbonate and forms oligomeric ether ketones at 300 °C in diphenyl sulfone.[22] A similar reaction is believed to happen here at temperatures higher than 250 °C, which results in an imbalance of stoichiometry and the formation of low molecular weight oligomers. Another side reaction at higher temperatures is due to the easy reduction of the thioanion, which tends to react with the sulfone group. Generally, we started the polymerization at 200 °C, and then raised the temperature to 240 °C.





Scheme 8.5. One-pot polymerization of N,N'-dimethyl-S-carbamate masked arylene dithiols with acitivated dihalo aromatic compounds

8.5. Poly(arylene thioether)s containing the fluorene or hexafluoroisopropylidene moieties.

A series of poly(arylene thioether)s containing fluorene and hexafluoroisopropylidene groups have been prepared by a one-pot polymerization reaction and characterized. As expected, they are all amorphous polymers with high glass transition temperatures (T_gs) and high thermal stabilities. They are readily soluble in $CHCl_3$, DMF, DMAc, and NMP.

Table 8.1. Properties of poly(arylene thioether)s containing the fluorene or hexafluoroisopropylidene moieties.

Polymer	M_w [a]	M_n [a]	η_{inh} [b] (dL/g)	T_g (°C) [c]	*TGA* (°C) [d]
8.9Ia	38,000	20,000	0.32	272	473
8.9Ib	41,000	23,000	0.32	239	516
8.9Ic	83,000	31,000	0.39	220	480
8.9Id	170,000	42,000	0.37	288	514
8.9Ie	ND [e]	ND [e]	0.39	268	509
8.9IIa	39,000	24,000	0.30	181	489
8.9IIb	59,000	32,000	0.33	157	514
8.9IIc	90,000	47,000	0.63	161	503
8.9IId	80,000	40,000	0.44	244	516
8.9IIe	ND [e]	ND [e]	0.56	191	524

a. Apparent molecular weights from GPC using polystyrene standards. The eluent was chloroform and the flow rate was 1 mL/min.

b. 5 g/dL in $CHCl_3$ at 25.0 °C.

c. Obtained by DSC under nitrogen atmosphere with heating rate of 20 °C.

d. 5 % weight loss temperature.

e. Not obtained.

The apparent molecular weights of these polymers were obtained by gel permeation chromatography (GPC) using polystyrene standards and they are listed in Table 8.1. The molecular weights of phenylphosphine oxide containing polymers **8.9Ie** and **8.9IIe** are not obtainable by GPC although they are very soluble in

chloroform. In all cases, high molecular weight polymers were obtained. Transparent and flexible films can be cast from chloroform solutions. The inherent viscosities (η_{inh}) of these polymers range from 0.30 to 0.63 dL/g in $CHCl_3$ solutions at 25 °C.

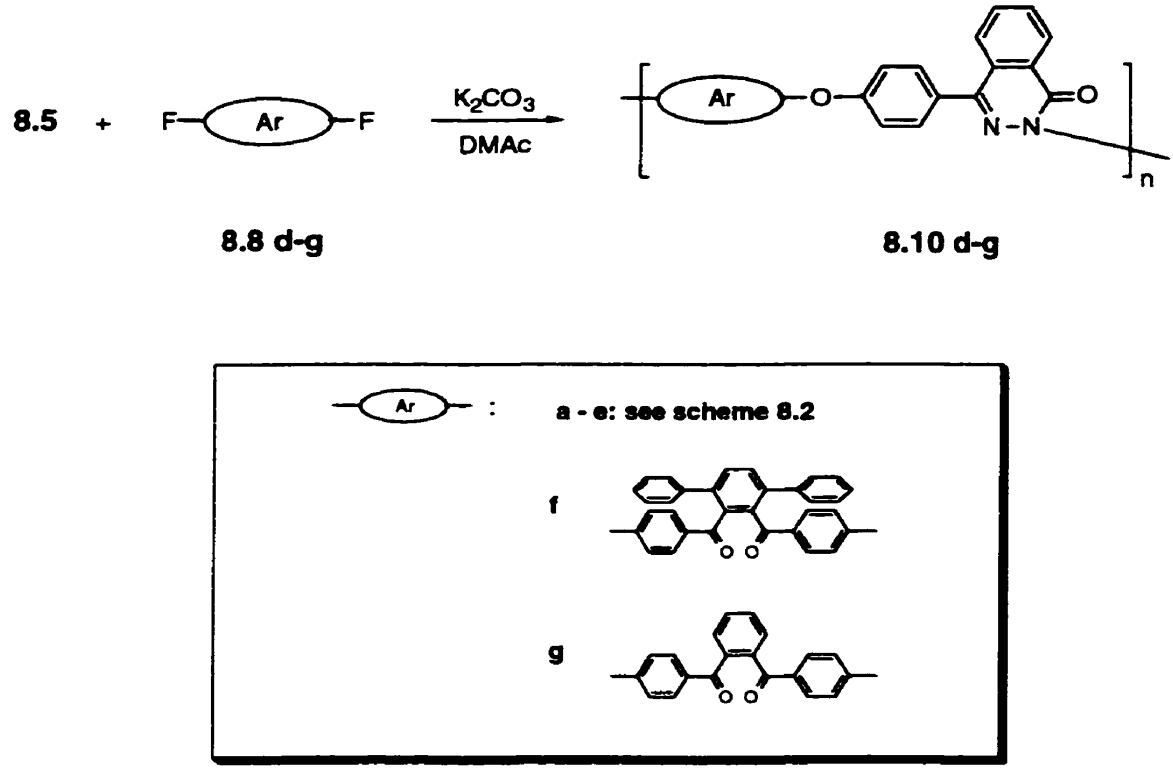
The thermal properties of these polymers were determined in differential scanning calorimeter (DSC) and thermogravimetric analysis (TGA) instruments and the results are listed in Table 8.1. These polymers have high Tgs and very high thermal stabilities. The T_g of fluorene containing poly(thioether)s range from 220 - 288 °C. Polymer **8.9Id** has the highest T_g and polymer **8.9Ic** has the lowest T_g among this series of polymers. The T_g of hexafluoroisopropylidene group containing polymers range from 157 - 244 °C. Polymer **8.9IId** has the highest T_g and polymer **8.9IIb** has the lowest T_g among this series of polymers. The glass transition temperatures of the poly(thioether)s are several degrees lower than their polyether analogs. For example, polymers **8.9Ia**, **8.9Ib**, and **8.9Ic** have T_gs of 272 °C, 239 °C, and 220 °C, respectively, while their polyether analogs have T_gs of 280 °C, 252 °C, and 223 °C, respectively.[16]

The 5 % weight loss temperatures in nitrogen atmosphere of these poly(thioether)s are greater than 473 °C (Table 8.1). Generally, the hexafluoroisopropylidene group containing polymers have higher thermal stabilities than the fluorene containing polymers. For example, the 5 % weight loss temperature of polymer **8.9Ic** is 480 °C, while that of polymer **8.9IIc** is 503 °C.

8.6. Poly(arylene ether)s containing the 1,2-dihydro-4-phenyl(*2H*)phthalazinone moiety

Monomer **8.5** forms poly(arylene ether)s with extremely high glass transition temperatures.[14,15] This unexpected property has been rationalized by its rigidity which can be seen in molecular models.[15] Another very interesting diketone monomer developed in this laboratory, 1,2-bis(4-fluorobenzoyl)-3,4,5,6-tetraphenyl (**8.8d**), also gave polymers with high glass transition temperatures.[23,24] Copolymers between **8.5** and **8.8d** would be expected to have very high T_gs. The syntheses of poly(arylene ether)s containing the 1,2-dihydro-4-phenyl(*2H*)phthalazinone moiety are shown in Scheme 8.6. As expected, high molecular weight polymers were readily synthesized by copolymerization of **8.5** with a series of activated dihaloaromatic compounds. They are all amorphous and very soluble in chloroform, DMAc, DMF, NMP, *etc.* The apparent molecular weights of these polymers were measured by GPC

and are listed in Table 8.2. The inherent viscosities of these polymer in chloroform are in the range of 0.33 - 0.64 dL/g, indicating they are high molecular weight.



Scheme 8.6. Synthesis of poly(arylene ether)s from monomer **8.5**

The thermal properties of polymers **8.10d-g** were measured by DSC and TGA analyses and are listed in Table 8.2. Polymer **8.10d** has a T_g of 320 °C, which is 7 °C higher than that of polymer from 9,9'-bis(4-hydroxyphenyl)fluorene and 28 °C higher than that of polymer from 4,4'-dihydroxybiphenyl.[23] For polymers **8.10d,** and **8.10f-g**, the T_g decreases as the number of phenyl substituents decreases in the diketone monomers. Polymer **8.10e,** which contains the triphenylphosphine oxide moiety, has a T_g of 309 °C. To the best of our knowledge, this polymer has the highest T_g among all of the poly(arylene ether)s containing the phenylphosphine oxide moiety previously reported.[25-27] A comparison of T_gs of different poly(arylene ether)s containing the phenylphosphine oxide moiety is shown in Scheme 8.7. The 5 % weight loss temperatures of these four polymers measured in nitrogen atmosphere are in the range of 473 °C to 517 °C, indicating their high thermal stabilities. Considering

the high T_g, high thermal stability, and the ability to resist an oxygen plasma and flame provided by the phenylphosphine oxide moiety, polymer **8.10e** should be a very interesting and promising candidate for materials used in aerospace.

Table 8.2. Properties of poly(arylene ether)s containing the 1,2-dihydro-4-phenyl(*2H*)phthalazinone moiety

Polymer	M_w[a]	M_n[a]	η_{inh}[b](dL/g)	T_g(°C)[c]	*TGA* (°C)[d]
8.10d	1,300,000	238,000	0.42	320	517
8.10e	ND[e]	ND[e]	0.33	309	512
8.10f	961,000	134,000	0.51	270	479
8.10g	200,000	19,000	0.64	241	473

a. Apparent molecular weights from GPC using polystyrene standards. The eluent was chloroform and the flow rate was 1 mL/min.

b. 5 g/dL in $CHCl_3$ at 25.0 °C.

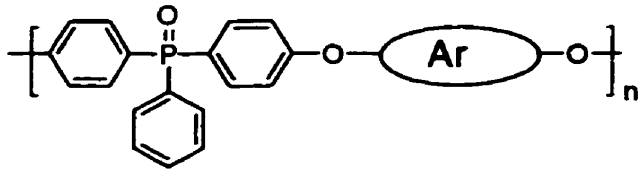
c. Obtained by DSC under nitrogen atmosphere with heating rate of 20 °C.

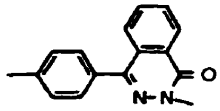
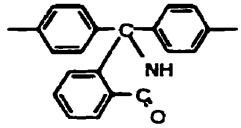
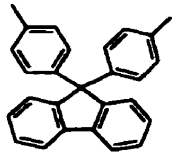
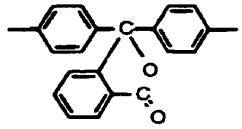
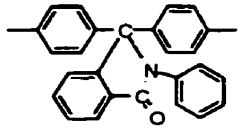
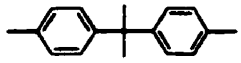
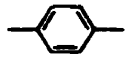
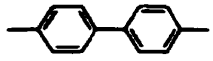
d. 5 % weight loss temperature.

e. Not obtained.

8.7. Poly(arylene thioether)s containing the 1,2-dihydro-4-phenyl(*2H*)phthalazinone moiety

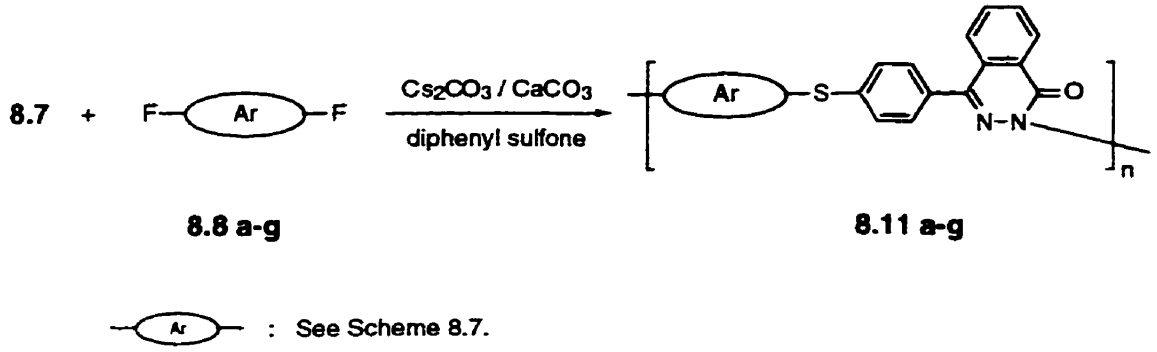
The synthesis of poly(arylene thioether)s containing the 1,2-dihydro-4-phenyl(*2H*)phthalazinone moiety is shown in Scheme 8.8. The polymerization reaction was carried out in diphenyl sulfone in the presence of a cesium carbonate and calcium carbonate mixture. The polymerization temperature was in the range of 200 - 240 °C. Generally, the polymerization reaction was started at 200 °C and then the temperature was gradually raised to 240 °C. Higher reaction temperatures are undesirable and should be avoided, because the thiophenoxide anion tended to react with sulfone group and high molecular weight polymers could not be obtained at the higher temperatures.



Ar	T_g (°C)	Reference
	309	this work
	294	15
	282	16
	279	15
	273	15
	205	16
	215	16
	245	16

Scheme 8.7. Comparison of T_gs for poly(arylene ether)s containing the phenylphosphine oxide moiety

The polymerization reaction proceeds by two different types of reaction. One is a N-C coupling reaction and the other one is a one-pot coupling reaction between S-(N,N'-dimethyl carbamate) and activated halo compounds. Toluene was not used here and the water formed during the reaction was removed by a stream of nitrogen. High molecular weight polymers were obtained in 3 - 4 h.



Scheme 8.8. Synthesis of poly(arylene thioether)s by a one-pot polymerization reaction between **8.7** and activated dihaloaromatic compounds

The apparent molecular weights of the polymers obtained were determined by GPC using polystyrene standards. These molecular weights are listed in Table 8.3. Although polymer **8.11e** is very soluble in chloroform, the molecular weight measurement could not be obtained on our GPC system. Presumably, this is because of the strong interactions between the column and the phenylphosphine oxide moiety. The inherent viscosities of these polymers measured in chloroform solutions are in the range of 0.30 to 0.59 dL/g. Transparent and creasable films can be cast from chloroform solution for all of the polymers.

All polymers obtained are amorphous and readily soluble in $CHCl_3$, DMF, DMAc, and NMP. The polymer from **8.5** and 4,4'-difluorobenzophenone has less solubility.[14] In comparison, polymer **8.11b** is very soluble, which may be due to the presence of the more flexible thioether linkage.

The thermal properties of these polymers were measured by DSC and TGA. The glass transition temperatures and 5 % weight loss temperatures under nitrogen atmosphere of these polymers are listed in Table 2. Compared with the poly(ether) analogs, poly(thioether)s have lower T_gs. For example, the polysulfone from **8.5** has a T_g of 294 °C, while polymer **8.11a** has a T_g of 244 °C. Among all of the polymers,

polymer **8.11d** has the highest T_g (303 °C) and the highest 5 % weight loss temperature as measured by TGA. Polymer **8.11c** has the lowest T_g, 217 °C.

Table 8.3. Properties of poly(arylene thioether)s containing the 1,2-dihydro-4-phenyl(*2H*)phthalazinone moiety

Polymer	M_w[a]	M_n[a]	η_{inh}[b](dL/g)	T_g(°C)[c]	*TGA* (°C)[d]
8.11a	39,000	16,000	0.30	244	472
8.11b	129,000	30,000	0.32	224	493
8.11c	538,000	61,000	0.59	217	491
8.11d	484,000	47,000	0.31	303	503
8.11e	ND[e]	ND[e]	0.30	293	503
8.11f	983,000	52,000	0.51	242	500
8.11g	1,623,000	138,000	0.38	230	469

a. Apparent molecular weights from GPC using polystyrene standards. The eluent was chloroform and the flow rate was 1 mL/min.

b. 5 g/dL in $CHCl_3$ at 25.0 °C.

c. Obtained by DSC under nitrogen atmosphere with heating rate of 20 °C.

d. 5 % weight loss temperature.

e. Not obtained.

8.8. Conclusions

A novel and convenient method to prepare poly(arylene thioether)s has been developed. High molecular weight poly(thioether)s were obtained from one-pot polymerization of bis(N,N'-dimethyl-S-carbamate)s with activated dihaloaromatic compounds in diphenyl sulfone in the presence of a cesium carbonate and calcium

carbonate mixture at 200 - 240 °C. Several advantages are associated with this novel polymerization reaction. Many monomers can be conveniently prepared from readily available dihydroxy aromatic compounds and the monomers are stable and easy to purify. Furthermore, the handling of oxidatively unstable and unpleasant smelling arylene dithiols is avoided. By using the present polymerization reaction, a wide variety of poly(arylene thioether)s can be readily synthesized. A series of poly(arylene thioether)s containing fluorene and hexafluoroisopropylidene moieties have been prepared which were characterized by GPC, DSC, TGA and inherent viscosity. These polymers are amorphous and have high glass transition temperatures and high thermal stabilities. The T_gs of the polymers are above 157 °C and 5% weight loss temperatures are above 473 °C. The inherent viscosities of these polymers are in the range of 0.30 - 0.63 dL/g.

The hydroxy group of the potentially inexpensive monomer, 1,2-dihydro-4-(4-hydroxyphenyl)(*2H*)phthalazin-1-one, has been selectively transformed into the N,N'-dimethylthiocarbamate group. The resulting N,N'-dimethylthiocarbamate has been converted into the S-(N,N'-dimethylcarbamate) **8.7** *via* the Newman-Kwart rearrangement reaction at 220 °C in diphenyl ether solution. A series of poly(arylene ether)s have been synthesized by copolymerization of **8.5** with a series of activated dihaloaromatic compounds in DMAc in the presence of anhydrous potassium carbonate. These polymers have very high glass transition temperatures and high thermal stabilities. Another series of poly(arylene thioether)s have also been synthesized by copolymerization of monomer **8.7** with a series of activated dihaloaromatic compounds in diphenyl sulfone solution in the presence of a cesium carbonate and calcium carbonate mixture at 200 - 240 °C. Two types of reaction are involved in this polymerization reaction. One is a N-C coupling reaction and the other one is a one-pot coupling reaction between S-(N,N'-dimethyl carbamate) and activated halo compounds. The poly(arylene thioether)s also have very high glass transition temperatures and high thermal stabilities.

8.9. Experimental section

Measurements

DSC analyses were conducted on a Seiko 220 DSC instrument at a heating rate of 20 °C/min in N_2 atmosphere (160 mL/min). The 5 % weight loss data were obtained from a Seiko 220 TG/DTA at a heating rate of 20 °C/min in N_2. GPC analyses were performed on a Waters 510 HPLC equipped with 4 phenogel columns (1 x linear, 3 x 500 Ä). $CHCl_3$ was used as the eluent and the UV detector was set at 254 nm.

Inherent viscosities were measured in $CHCl_3$ at 25.0 ± 0.1 °C using a Ubbelohde viscometer. HPLCs were performed on a Milton Roy CM4000 system equipped with a Lichrosphere 5 RP18e reverse phase column and methanol was used as the eluent. NMR spectra were recorded on a Varian Unity 500 instrument in $CDCl_3$ solution. TMS was used as reference for ^{1}H-NMR and the solvent, $CDCl_3$, was used for ^{13}C-NMR. Melting points were taken on a Fisher-Johns melting point apparatus and the thermometer was uncorrected.

Materials

8.1I, **8.1II**, and N,N'-dimethyl thiocarbamoyl chloride were obtained from commercial sources and used as received. **8.8a**, **8.8b**, cesium carbonate and fine grade calcium carbonate were used without purification. Monomers **8.8c**,[28] **8.8d**,[23] **8.8e**[29] were prepared according to previously reported methods. The monomer **8.5** was synthesized from phenolphthalein (**8.4**) by the previously described method. (Scheme 8.2)[14,15] Diphenyl sulfone was purchased from Aldrich Chemical Inc. and recrystallized from ethanol prior to use. DMAc, toluene, chloroform, methanol and acetone were used as received.

Preparation of 8.2I.

Bisphenol **8.1I** (20.0 g, 0.057 mol) was added to 100 mL of an ice cold KOH methanolic (7.3 g, 0.13 mol) solution and stirred at 0 °C for 0.5 h. N,N'-Dimethylthiocarbamoyl chloride (15.5 g, 0.125 mol) was then added in one portion and the mixture was stirred for another 2 h. The precipitated white solid was collected by filtration and washed with ice-cold methanol : water (1 : 1) (150 mL). A white solid **8.2I** (25.4 g, yield 85 %) was obtained after recrystallization from $CHCl_3$/methanol. M.p. 239 - 241 °C. ^{1}H-NMR ($CDCl_3$): δ (ppm) 7.75 (d, 2H, J = 7.6 Hz), 7.41 (d, 2H, J = 7.6 Hz), 7.34 (t, 2H, J = 7.6 Hz), 7.25 (t, 2H, J = 7.6 Hz), 7.22 (d, 4H, J = 8.6 Hz), 6.92 (d, 4H, J = 8.6 Hz), 3.42 (s, 6H), 3.28 (s, 6H). ^{13}C-NMR ($CDCl_3$): δ (ppm) 187.4, 152.7, 150.9, 143.1, 140.0, 128.9, 127.8, 127.6, 126.2, 122.3, 120.1, 64.6, 43.2, 38.6. MS: *m/z* 524 (M^+, 38), 437(15), 88(100), 72(80). HRMS: found, 524.1595; calcd for $C_{31}H_{28}N_2O_2S_2$, 524.1592.

Preparation of 8.2II.

Bisphenol **8.1II** (20.0 g, 0.06 mol) was added to 100 mL of ice cold methanolic KOH (7.3 g, 0.13 mol) solution and stirred at 0 °C for 0.5 h. N,N'-Dimethylthiocarbamoyl chloride (16.3 g, 0.13 mol) was then added and the mixture was stirred for another 2 h. The precipitated white solid was collected by filtration and washed with ice-cold methanol : water (1 : 1) (150 mL). A white solid **8.2II** (26.8 g, yield 88 %) was obtained after recrystallization from $CHCl_3$/methanol. M.p. 213 - 215 °C. ^{1}H-NMR ($CDCl_3$): δ (ppm) 7.44 (d, 4H, J = 8.3 Hz), 7.10 (d, J = 8.3 Hz), 3.46 (s, 6H), 3.34 (s, 6H). ^{13}C-NMR ($CDCl_3$): δ (ppm) 186.8, 154.2, 131.1, 130.4, 122.6, 43.2, 38.7. MS: *m/z* 510(M^+, 28), 423(7), 88(100), 72(97). HRMS: found, 510.0873; calcd for $C_{21}H_{20}F_6N_2O_2S_2$, 510.0870.

Preparation of 8.3I.

The mixture of **8.2I** (20.0 g) and diphenyl ether (15.0 g) was heated at 260 °C under N_2 atmosphere for 2 h. The cooled mixture was washed with 150 mL of methanol to obtain the crude product. After recrystallization from a $CHCl_3$/ methanol mixture, a white solid **8.3I** (14.8 g, yield 74 %) was obtained. M.p. 279 - 280 °C. ^{1}H-NMR ($CDCl_3$): δ (ppm) 7.74 (d, 2H, J = 7.3 Hz), 7.3 (m, 14H), 3.0 (d, 12H). ^{13}C-NMR ($CDCl_3$): δ (ppm) 166.8, 150.3, 146.6, 140.1, 135.5, 128.7, 127.9, 127.7, 127.0, 126.2, 120.2, 65.1, 36.9. MS: *m/z* 524(M^+, 33), 453(8), 72(100). HRMS: found, 524.1596; calcd for $C_{31}H_{28}N_2O_2S_2$, 524.1592.

Preparation of 8.3II.

8.2I (15.0 g) was placed in a 100 mL of round bottom flask and heated at 260 °C under N_2 atmosphere for 2 h. After recrystallization from methanol/water, a white solid **8.3II** (13.2 g, yield 88 %) was obtained. M.p. 138 - 139 °C. ^{1}H-NMR ($CDCl_3$): δ (ppm) 7.51 (d, 4H, J = 8.5 Hz), 7.41 (d, J = 8.5 Hz), 3.10 (s, 6H), 3.04 (s, 6H). ^{13}C-NMR ($CDCl_3$): δ (ppm) 166.0, 135.1, 133.8, 130.5, 130.5, 36.9. MS: *m/z* 510(M^+, 56), 72(100). HRMS: found, 510.0874; calclcd for $C_{21}H_{20}F_6N_2O_2S_2$, 510.0870.

Preparation of 8.6.

8.5 (23.8 g, 0.1 mol) was added to 400 mL of ice-cold methanol solution which contained 6.2 g (0.11 mol) of potassium hydroxide. The mixture was stirred at

0 °C for 1/2 h and then N,N'-dimethylthiocarbamoyl chloride (13.53 g, 0.11 mol) was added. After stirring for another 2 h, the precipitate was collected by filtration and washed with cold methanol-water (200 mL). Pure white solid **8.6** (18.2 g, yield 56 %) was obtained after recrystallization from DMF. M.p. 268 - 269 °C. ^{1}H-NMR (DMSO-*d* 6): δ (ppm) 12.9 (s, 1H, NH), 8.36 (d, 1H, J = 7.3 Hz), 7.94 (m, 2H), 7.70 (d, 1H, J = 7.3 Hz), 7.63 (d, 2H, J = 8.3 Hz), 7.26 (d, 2H, J = 8.3 Hz), 3.41 (s, 3H), 3.37 (s, 3H). ^{13}C-NMR (DMSO-*d* 6): δ (ppm) 186.1, 159.2, 154.2. 145.7, 133.6, 132.4, 131.6, 130.2, 128.9, 127.9, 126.4, 126.1, 42.8, 38.6. MS: *m/z* 350(M^+, 55), 238(60), 88(100), 72(82). HRMS: found, 325.0883; calcd for $C_{17}H_{15}N_3O_2S$, 325.0885.

Preparation of 8.7.

The mixture of **8.6** (17.8 g, 0.55 mol) and diphenyl ether (15.0 g) was placed in a salt bath preheated to 220 °C for 3 h under nitrogen atmosphere. After cooling down, the solid was first washed with 100 mL of methanol and then recrystallized from DMF. Pale yellow crystals of **8.7** (14.7 g, yield 83 %) were obtained. M.p. 273 - 274 °C. ^{1}H-NMR (DMSO-*d* 6): δ (ppm) 12.9 (s, 1H, NH), 8.36 (d, 1H, J = 7.4 Hz), 7.91 (m, 2H), 7.70 (d, 1H J = 7.4 Hz), 7.6 (m, 4H), 3.1 (s, 3H), 3.0 (s, 3H). ^{13}C-NMR ($CDCl_3$): δ (ppm) 164.6, 159.2, 145.6, 135.6, 135.4, 133.6, 131.7, 129.8, 129.6, 128.8, 127.9, 126.3, 126.1, 36.5. MS: *m/z* 325(M^+, 46), 238(44), 88(14), 72(100). HRMS: found, 325.0882; calcd for $C_{17}H_{15}N_3O_2S$, 325.0885.

General procedure for polymerization of 8.3I with activated dihalocompounds.

A typical example is given as follows. To a 25 mL three neck flask equipped with magnetic stirrer and a N_2 inlet, **8.3I** (1.0494 g, 2.0 mmol), bis(4-fluorophenyl) sulfone (0.5085 g, 2.0 mmol), cesium carbonate (0.32 g, 1.0 mmol), calcium carbonate (0.60 g, 6.0 mmol) and 5.0 g of diphenyl sulfone were charged. The mixture was brought up to 200 °C and kept at that temperature for 2 h. Then, an additional 2.0 g of diphenyl sulfone was added to dilute the solution and the reaction temperature was brought up to 240 °C and kept at that temperature for another 2 h. The mixture was cooled down and dissolved in 15 mL of $CHCl_3$. The $CHCl_3$ solution was poured into 150 mL of acetone to precipitate out the polymer which was collected by filtration. The polymer was redissolved in $CHCl_3$ and filtered through a thin layer of

celite and reprecipitated out by pouring into methanol. The polymer was collected and dried at 100 °C in vaccuo for 24 h.

General procedure for polymerization of 8.3II with activated dihalocompounds.

The polymerization was carried out as above. The mixture was then diluted with 15 mL of $CHCl_3$ and poured into 150 mL of hot methanol to precipitate out the polymer. The crude polymer was dissolved in 20 mL of $CHCl_3$ and filtered through a thin layer of celite. The $CHCl_3$ solution was poured into 150 mL of methanol to precipitate out fibrous polymer. The polymer was dissolved in $CHCl_3$ and poured into methanol once more to remove any remaining diphenyl sulfone. The polymer was collected and dried at 100 °C in vaccuo for 24 h.

General procedure for polymerization of 8.5 with activated dihalocompounds.

A typical example is given as follows. To a dry 50 mL three neck flask equipped with a Dean-Stark trap, water condenser, a magnetic stirrer and a nitrogen inlet, **8.5** (0.9530 g, 4.00 mmol), bis(4-fluorophenyl)phenylphosphine oxide (**9.5d**) (1.2571 g, 4.00 mmol), anhydrous potassium carbonate (1.10 g, 8.0 mmol), toluene (8 mL) and DMAc (10 mL) were charged. Under an atmosphere of nitrogen, the solution was heated and maintained at 140 °C for 2 h to remove all water by means of azotropic distillation with toluene. The temperature was then increased to 170 °C by removing the toluene and maintained at this temperature until the solution became very viscous. The resulting mixture was diluted with 5 mL of DMAc and poured into 200 mL of methanol to precipitate out the polymer. The white fibrous polymer was redissolved in 30 mL of chloroform and filtered through a thin layer of celite to remove the salt. After adding several drops of actetic acid to neutralize any remaining phenoxide end groups, the filtrate was then poured into a 200 mL of methanol to precipitate out polymer. The polymer was collected by filtration and dried at 100 °C in vaccuo for 24 h.

General procedure for polymerization of 8.7 with activated dihalocompounds.

A typical example is given as follows. To a 50 mL three neck flask equipped with magnetic stirrer and a nitrogen inlet, **8.7** (0.9768 g, 3.00 mmol), bis(4-fluorophenyl) sulfone (0.7628 g, 3.00 mmol), cesium carbonate (0.50 g, 1.50 mmol),

calcium carbonate (0.90 g, 9.0 mmol) and 6.0 g of diphenyl sulfone were charged. The mixture was brought up to 200 °C and kept at that temperature for 2 h. Then, an additional 2.0 g of diphenyl sulfone was added to dilute the solution and the reaction temperature was brought up to 240 °C and kept at that temperature for another 2 h. The mixture was cooled down and 20 mL of chloroform was added. The chloroform solution was poured into 200 mL of acetone to precipitate out the polymer which was collected by filtration. The polymer was redissolved in chloroform and filtered through a thin layer of celite to remove the salt and precipitated out by pouring into methanol. The polymer was collected and dried at 100 °C in vaccuo for 24 h.

8.10. References and notes

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Chapter 9. Synthesis, Characterization and Ring-opening Polymerization of Cyclic(arylene ether) Oligomers

9.1. Introduction

Macrocyclic oligomers as precursors of high performance polymers have received a great deal of attention[1-7] since the pioneering work of Brunelle *et al.* on macrocyclic carbonates.[8-10] Macrocycles can be processed at much lower temperature than the corresponding high molecular weight polymers since they have much lower melt viscosities, and they can undergo controlled ring-opening polymerization without liberation of byproducts. All of these advantages make them potentially applicable in the areas of advanced thermoplastic composites and high temperature adhesives. We have reported that poly(ether ketone)s containing the *o*-dibenzoylbenzene group are a class of soluble, amorphous high performance polymers with high T_gs and excellent mechanical properties.[11] An efficient method for the synthesis of macrocyclic procursors of this class of polymers containing 1,2-dibenzoyl benzene and 1,2-dibenzoyl-3,6-diphenylbenzene moieties has been developed in this laboratory using a high-dilution method by slow addition of reactants to the reaction mixture via a syringe pump. The macrocycles formed readily undergo ring opening to give linear high molecular weight polymers.[12,13] Polymers containing the tetraphenylbenzene moiety are also amorphous and are soluble in a variety of solvents and have significantly higher T_gs.[11,14] However, the corresponding macrocycles could not be easily prepared by the previously described method by addition of the reactions slowly to the reaction mixture via a syringe pump because the starting material, 1,2-bis(4-fluorobenzoyl)-3,4,5,6-tetraphenylbenzene (**9.1**) has low solubility in DMF at room temperature which is the preferred solvent for the reaction.[12]

High performance polymers containing the phenylphosphine oxide moiety have received extensive attention recently, since the presence of the phenylphosphine oxide moiety in the polymers provides nonflammability and oxygen plasma resistance while maintaining the high glass transition temperatures, high thermal stabilities and mechanical properties at the same time.[15-20] The synthesis of cyclic(arylene ether) oligomers containing the phenylphosphine oxide moiety provides new intermediates for the preparation of high performance polymers containing the phenylphosphine oxide

moiety. These cyclic oligomers themselves can be potentially used as flame retardants. They would have the advantages of better compatibility with base polymers and low migration compared with conventional organic flame retardants since the cyclic oligomers are relatively large molecules.

9.2. Strategy and goals

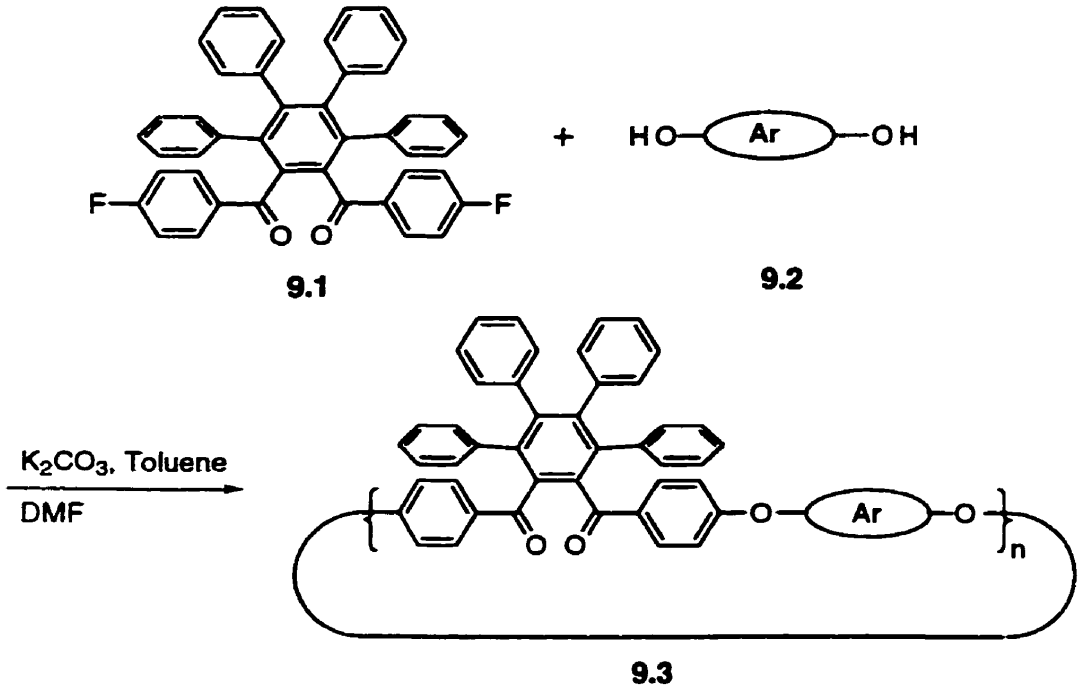
We attempted to achieve high-dilution reaction conditions by adding the reactants, **9.1** and bisphenol, in portions in solid form to the reaction mixture and we succeeded in synthesizing a series of new cyclic(arylene ether) oligomers containing the tetraphenylbenzene moiety. With these cyclic oligomers on hand, characterization and ring-opening polymerziation reaction were carried out.

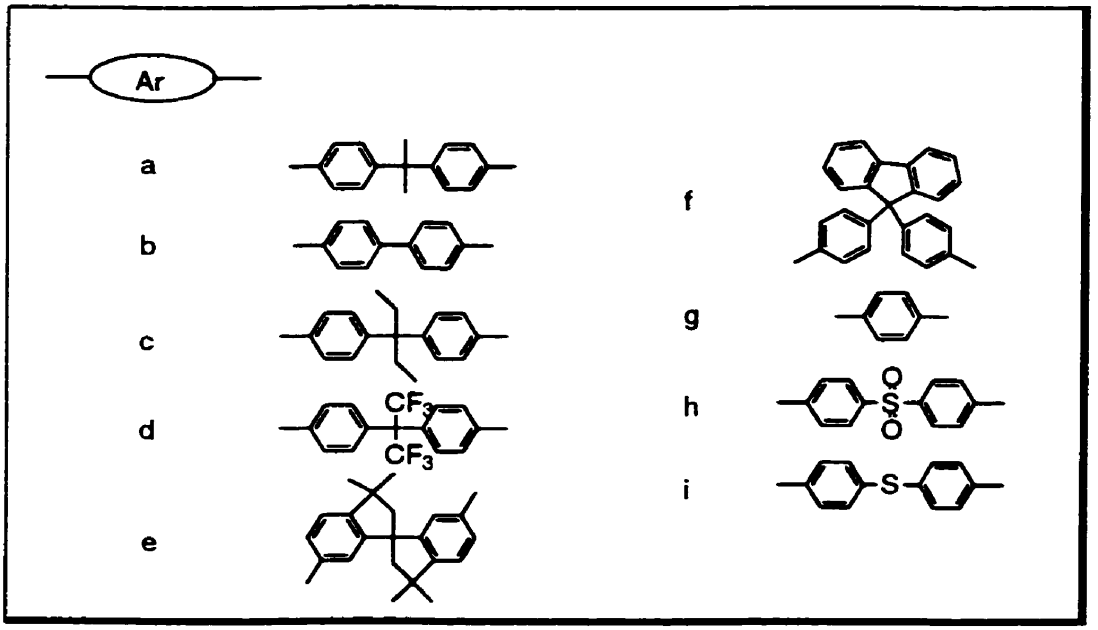
The synthesis of cyclic(arylene ether) oligomers containing the phenylphosphine oxide moiety were synthesized using the standard high dilution conditions.[12] The cyclic oligomers were characterized by GPC, MALDI-TOF-MS and themoanalyses. The ring-opening polymerization was carried by using potassium biphenoxide as the initiator.

9.3 Cyclic(arylene ether) oligomers containing the tetraphenylbenzene moiety.

9.3.1. Synthesis and characterization of cyclic(arylene ether ketone) oligomers containing the tetraphenylbenzene moiety.

Due to the low solubility of the starting material, 1,2-bis(4-fluorobenzoyl)-3,4,5,6-tetraphenylbenzene (**9.1**) in DMF, the reactants can not be delivered to the reaction vessel through a syringe pump. We were successful in achieving high-dilution reaction conditions by adding the reactants, 1,2-bis(4-fluorobenzoyl)-3,4,5,6-tetraphenylbenzene and bisphenol, in portions in solid form to the reaction mixture. The reactants were delivered in 10 portions over 9 h. This strategy gave us very high yields of cyclic(ether ketone)s containing the tetraphenylbenzene moiety (Table9.1). The reaction is shown in Scheme 9.1. If all the reactants were added to the reaction mixture in one portion, significant amounts of high molecular weight linear oligomers





Scheme 9.1. Preparation of cyclic(ketone ether)s containing the tetraphenylbenzene moiety.

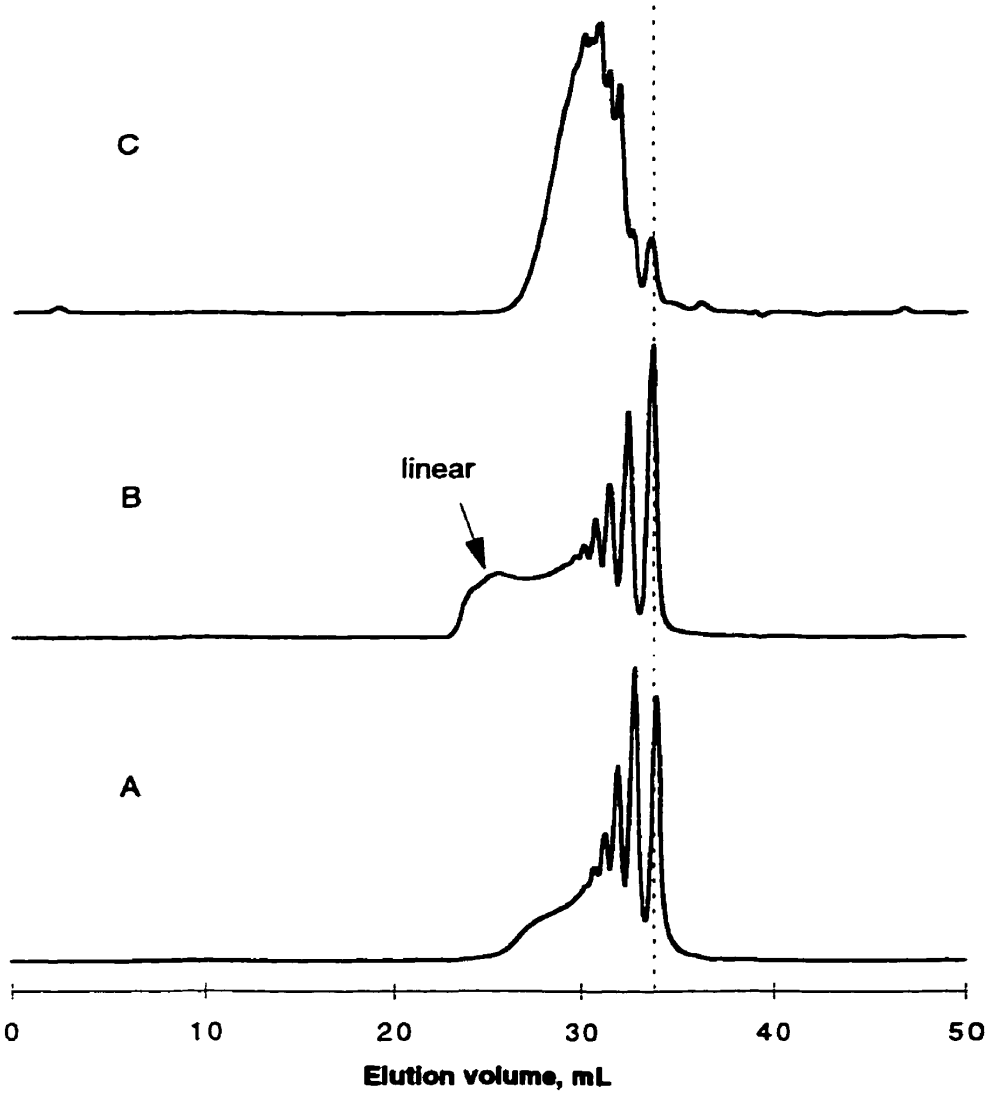


Figure 9.1. GPC charts. (A). Cyclic oligomers **9.3a** obtained by adding reactants in 10 portions; (B). Cyclic oligomers **9.3a** obtained by adding reactants in one portion; (C). Linear oligomers **9.4**.

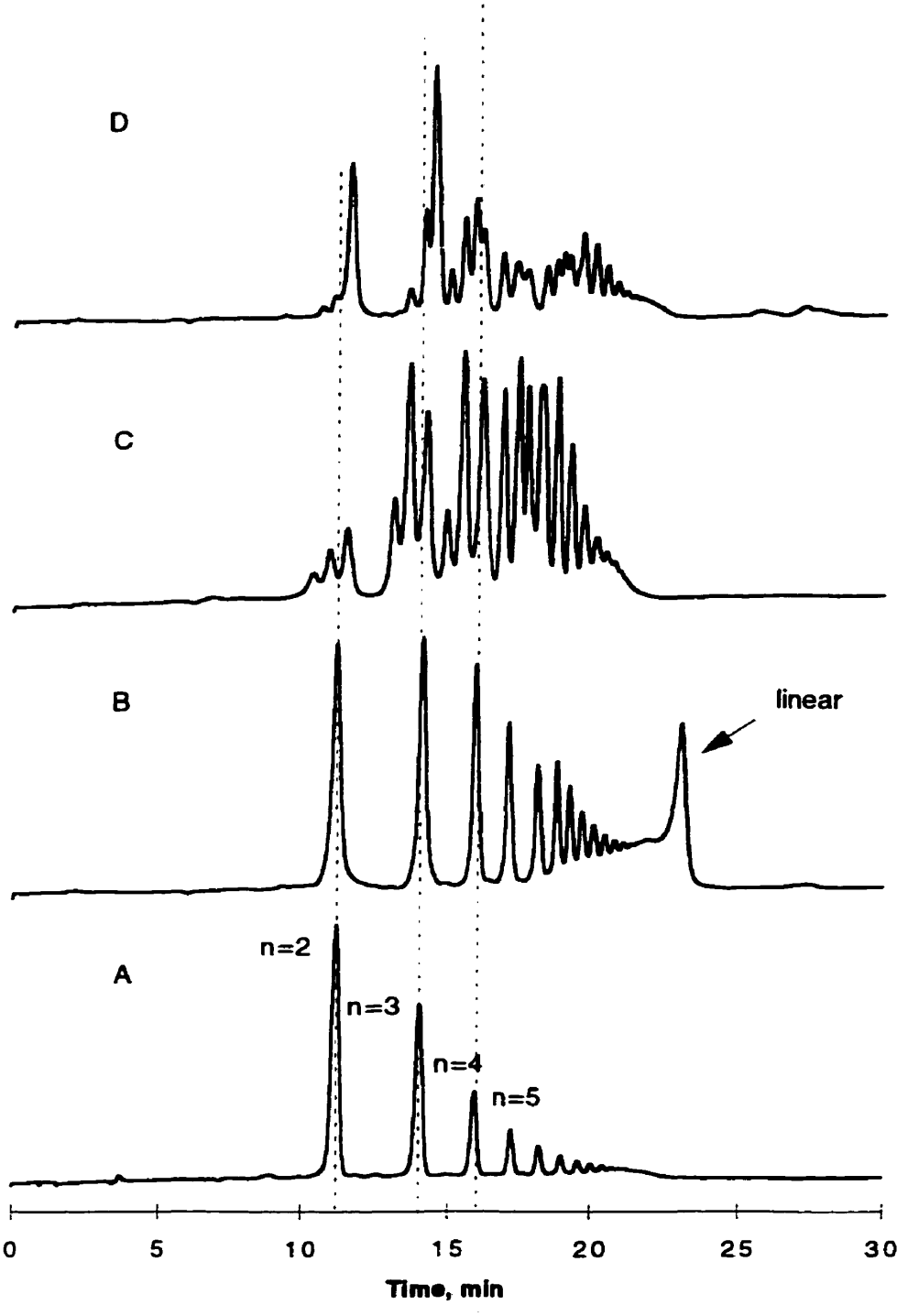
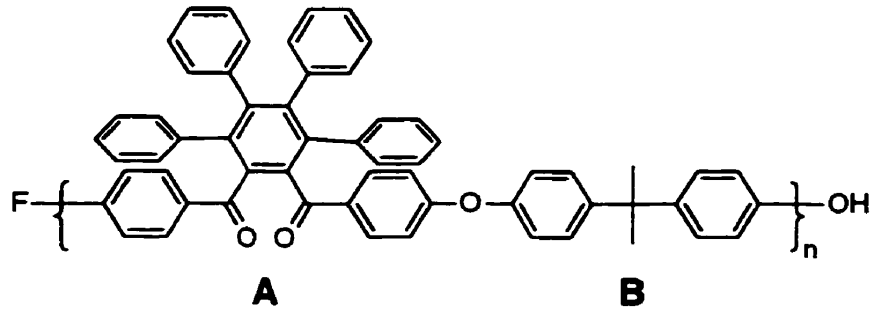


Figure 9.2. Gradient HPLC charts. (A). Cyclic oligomers **9.3a** obtained by adding reactants in 10 portions; (B). Cyclic oligomers **9.3a** obtained by adding reactants in one portion; (C). Linear oligomers **9.4**; (D) Mixture of equivalent amounts of cyclic oligomers **9.3a** and linear oligomers **9.4**.

were obtained (Figure 9.1,B and Figure 9.2,B). The lower yields of **9.3b** and **9.3g** (Table 9.2) are due to the lower solubilities of their dimers in DMF some of which were lost during work up. However, the low yield of **9.3h** can be attributed to the low reactivity of bis(4-hydroxyphenyl)sulfone in the nucleophilic displacement reaction. Electronegative sulfone groups significantly lower the reactivity of the phenoxide anion.

GPC and gradient HPLC methods were used to analyze the products. All of them showed that the major products were cyclic dimer, trimer and tetramer. Only small amounts of higher oligmers were formed. GPC results for macrocycles **9.3a** are shown in Figure 9.1. **9.3a** has a number average molecular weight of 2500 and a weight average molecular weight of 5200 calibrated against polystyrene standards. Analysis by gradient HPLC gave similar results. The gradient conditions were as follows: at 0 min, THF 70%, H_2O 30%; at 20 min, THF 90%, H_2O 10%; at 22 min, THF 100%; at 25 min , THF 100%; at 27 min, THF 70%, H_2O 30%; at 30 min (end), THF 70%, H_2O 30%. Generally, cyclic(ether ketone)s made by this method consist of around 35% dimer, 20% trimer , 12% tetramer and 7% pentramer.



9.4

To be convinced the products we obtained were cyclic oligomers, an authentic linear oligomer sample **9.4** was synthesized and comparation studies were made between linear oligomers **9.4** and the cyclic oligomers **9.3a** obtained herein. The linear oligomers were synthesizedunder typical polymerization conditions by stopping the reaction at an early stage. The number average molecular weight of this linear oligomer sample is 3200 and weight average molecular weight is 4300 analysized by GPC which are comparable with the molecular weights of the cyclic oligomers **9.3a** (Figure 9.1). It is anticipated that three types of linear oligomers are possible: $A(BA)_{n-1}B$, $(BA)_{n-1}B$, $A(BA)_{n-1}BA$. Gradient HPLC analysis shows this

distribution pattern (Figure 9.2, C). The gradient HPLC was also taken for the mixture of equivalent amounts of cyclic oligomers **9.3a** and linear oligomers **9.4** (Figure 9.2, D). These HPLC profiles shown in Figure 9.2 indicate that linear oligomers can be easily detected by the used gradient HPLC conditions. The gradient HPLC of the cyclic oligomers shows no evidence of linear oligomers.

^{1}H-NMR and ^{19}F-NMR were taken for all the samples and no hydroxy and/or fluoro end groups were detected in these studies, though these end groups are easily detected for the linear oligomers. A comparison of ^{19}F-NMR between linear oligomers **9.4** and cyclic oligomers **9.3a** is shown in Figure 9.3. NMR studies confirmed the cyclic nature of these samples.

The most powerful tool for analysis of the cyclics is MALDI-TOF-MS. Dithranol was chosen as the matrix for the analysis. Without the addition of a silver compound as a cationization agent, the mass spectra were not clean and difficult to interpret. Even with addition of sodium salt, the spectra were still difficult to interpret. However, when a silver salt was added, the mass spectra were much cleaner. Generally, we can see macrocyclics with repeating units up to 8 or 9 units. The MALDI-TOF-MS of cyclic oligomers **9.3a** is shown in Figure 9.4. The perfect match of measured mass with the calculated mass of cyclics (Table 9.1) also confirmed the cyclic properties. In Table 9.1, peak intensities are reported relative to the strongest molecular peak. Comparing Figure 9.2 with Figure 9.5, we can see that MALDI-TOF-MS gives almost the same distribution pattern as gradient HPLC. However, for composition analysis of cyclics, gradient HPLC is much preferred. The MALDI-TOF-MS of linear oligomers **9.4** is shown in Figure 9.5. In this spectrum, three different kinds of linear oligomer peaks are clearly and unambiguously shown, which are also suggested by gradient HPLC. The spectrum also indicates that the cyclic linear oligomers contains small amount of cyclic dimer and trimer. By comparing Figure 9.4 and 9.5, one can easily draw the conclusion that the oligomers obtained by the present method are exclusively cyclics.

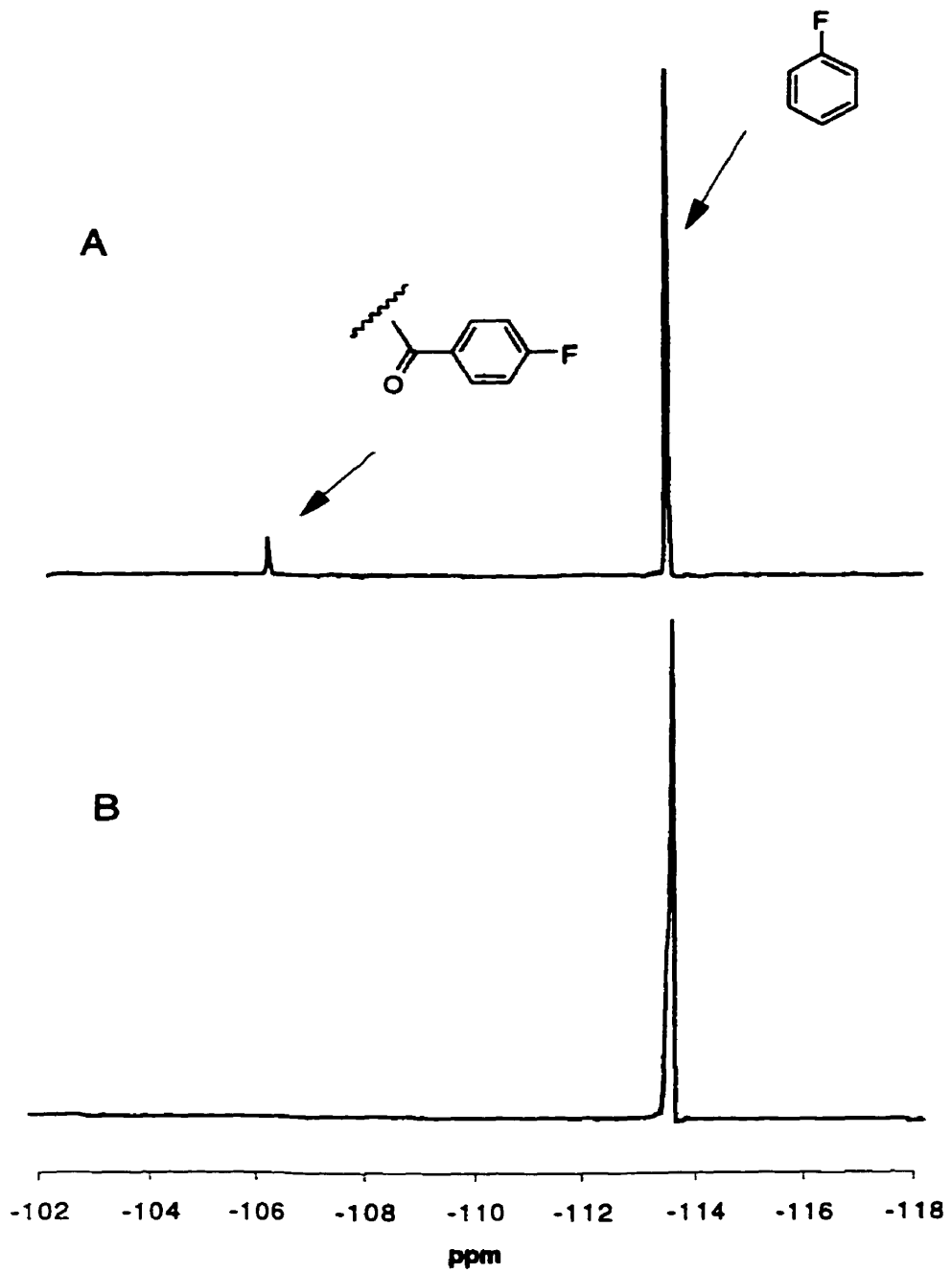


Figure 9.3. ^{19}F-NMR of cyclic oligomers **9.3a** and linear oligomers **9.4**. (A). Linear oligomers; (B). Cyclic oligomers.

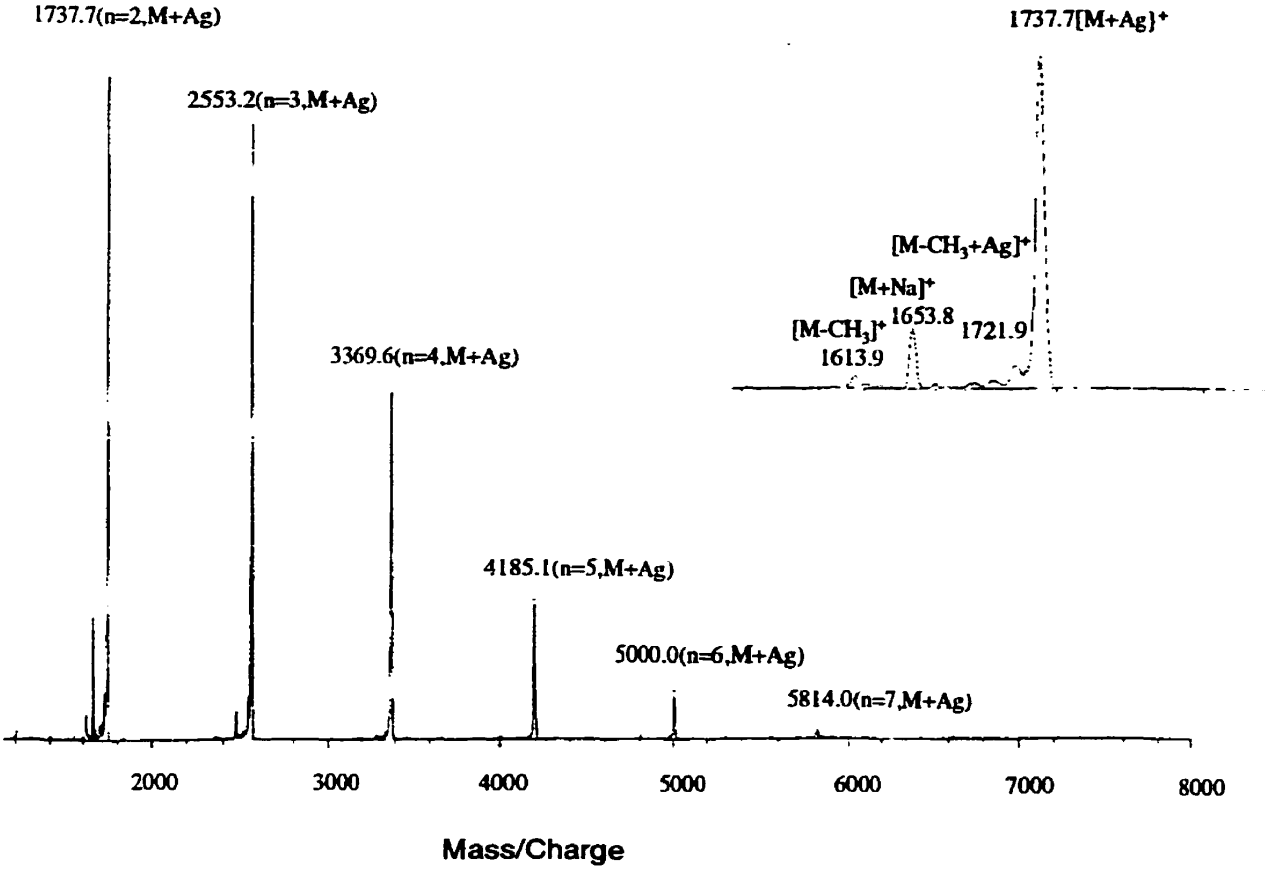


Figure 9.4. MALDI-TOF-MS of cyclic oligomers **9.3a**

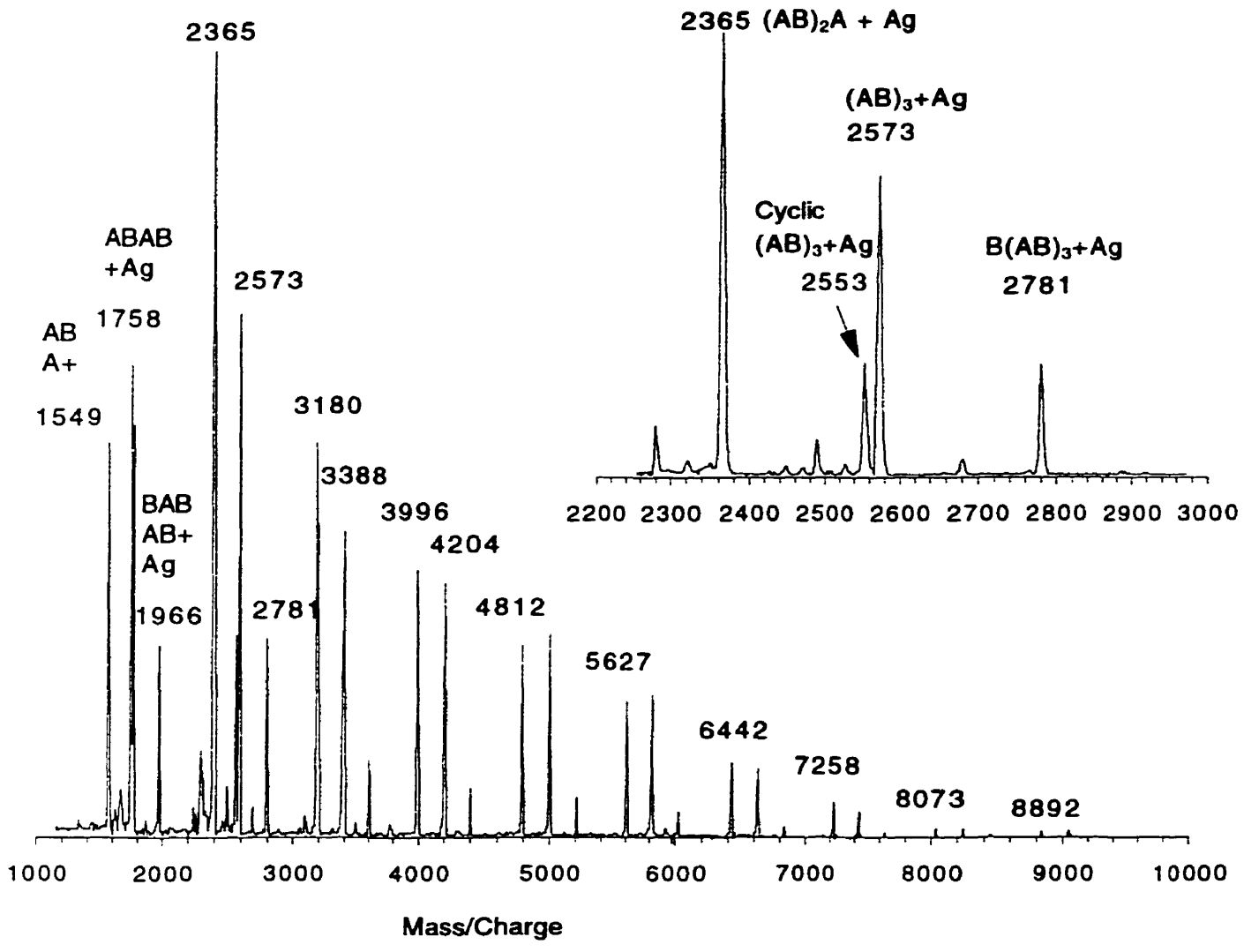


Figure 9.5. MALDI-TOF-MS of linear oligomers **9.4.** A-Tetraphenyldiketone moiety; B-BPA moiety.

Table 9.1. MALDI-TOF-MS analyses of cyclic(ether ketone) oligomers (g/mol).

		M1+Ag	M2+Ag	M3+Ag	M4+Ag	M5+Ag	M6+Ag	M7+Ag	M8+Ag
	Meas.		1737.7	2553.2	3369.6	4185.1	5000	5814	
9.3a	Calc.		1738	2553	3368	4183	4998	5813	
	Intensity		100	93	53	20	7	1	
	Meas.		1653.8	2426.6	3199.8	3973.1	4747	5521.4	6289.4
9.3b	Calc.		1653.6	2624.4	3199.3	3972.1	4745	5517.8	6290.6
	Intensity		92	100	66	42	17	6	2
	Meas.		1793.5	2636.8	3480.3	4322.4	5167.3		
9.3d	Calc.		1794	2637	3480	4323	5166		
	Intensity		100	45	20	7	2		
	Meas.	1002.6*	1898	2794.8	3690	4585			
9.3e	Calc.	1003	1898	2793	3688	4583			
	Intensity	61	100	36	10	2			
	Meas.		1982	2919.9	3857.6	4795.2	5733.1	6673.2	
9.3f	Calc.		1982	2919	3856	4793	5730	6667	
	Intensity		100	56	28	10	3	1	
	Meas.		1502.1	2199.4	2897	3594.6	4293	4989.2	
9.3g	Calc.		1501	2198	2895	3592	4288	4985	
	Intensity		50	100	56	25	13	2	
	Meas.		1782	2619.7	3456.6	4293			
9.3h	Calc.		1782	2619	3456	4292			
	Intensity		100	18	4	0.5			
	Meas.		1718.7	2524.2	3329.6	4137.1	4942.1		
9.3i	Calc.		1718	2523	3328	4132	4937		
	Intensity		100	46	21	8	3		

* Another molecular peak observed is M1 without silver attachment. Measured, 895.6, intensity, 83%, calculated, 895.

The X-ray structure of the cyclic dimer obtained by reaction of 1,2-bis(4-fluorobenzoyl)benzene and 4,4'-thiobiphenol has been resolved.[21] The cyclic property of the present series of macrocyclic oligomers can also be inferred from this data. The ease of formation of cyclics is attributed to the conformation of the diketone reactant. This can be seen from the molecular model of 1,2-bis(4-fluorobenzoyl)-3,4,5,6-tetraphenylbenzene shown in Figure 9.6 which was generated by a molecular mechanics calculation using the CAChe program on a Macintosh computer. The two fluoro atoms are in bent positions which facilate the formation of cyclics. In the case of **9.3e**, due to this bent conformation and, in addition, the bent conformation of the bisphenol, spirobiindanebisphenol (SBI), the cyclic monomer was the predominant product. This behavior is quite different from other cyclics in this series. The use of monomers such as SBI to facilitate the formation of cyclics has also been reported by other researchers.[6,10,22]

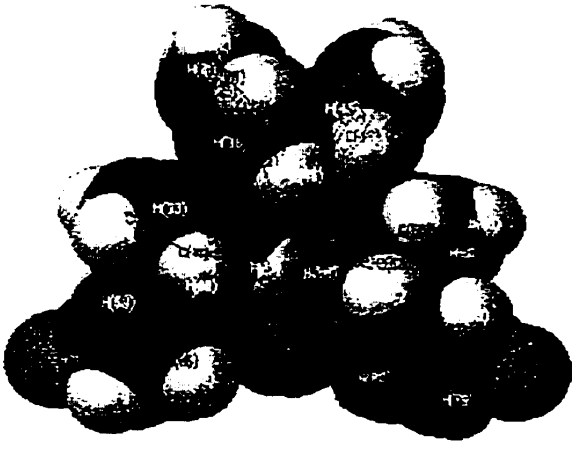


Figure 9.6. Stable conformation of 1,2-bis(4-fluorobenzoyl)-3,4,5,6-tetraphenylbenzene.

Table 9.2. Properties of cyclic(ether ketone)s containing the tetraphenylbenzene moiety

Cyclics	Yield(%)[a]	Mn[b]	Mw[b]	Tg(°C)[c]	Tm(°C)[c]	TGA(°C)[d]
9.3a	70	2500	5200	243(265)[e]	469	521
9.3b	64.1	2500	7000	267(292)[e]	-	487
9.3c	84	2200	4300	251	-	461
9.3d	85.1	1900	3300	254(278)[e]	394	507
9.3e	85	800	1100	379	430	467
9.3f	85	2000	3600	296(313)[e]	425	460
9.3g	65	2200	3700	260(273)[e]	354	457
9.3h	55	1600	2300	257	-	443
9.3i	90	2400	4800	236	377	466

a. Isolated yield.

b. Measured by GPC and calibrated against polystyrene.

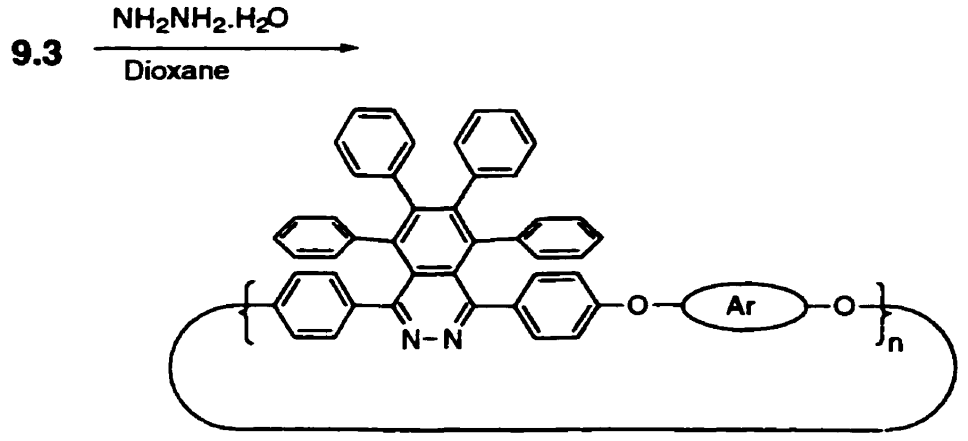
c. Measured under N_2 by DSC, heating rate was 20 °C/min.

d. Temperature at which 5% weight loss was observed under N_2 atmosphere, heating rate was 20 °C/min.

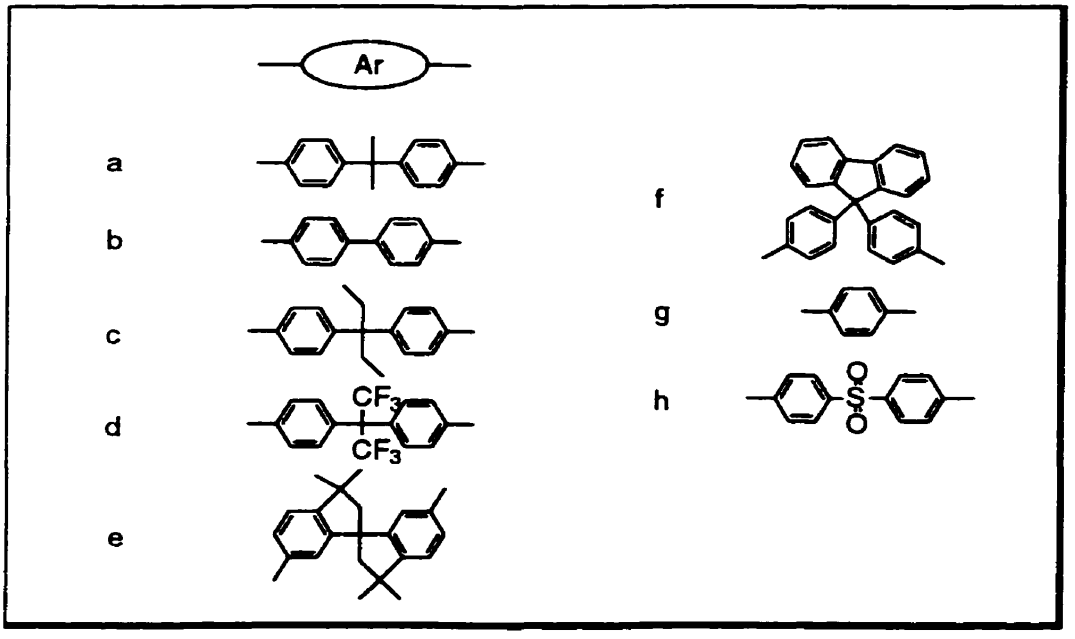
e. T_g of corresponding polymer.

As expected, all of the cyclic(ether ketone)s show T_gs higher than 230 °C. The T_gs of the macrocyclic oligomers are generally 13-25 °C lower than the linear analogs. The thermal properties of these cyclics are summarized in Table 9.2. The strong endothermic peaks of these cyclics correspond to melting points due to the high percentage of dimers and trimers which they contain. Although the melting points of these cyclics are very high, they readily flow above their T_ms. The very high T_ms of these cyclics would require the use of very high temperatures during the ring-opening polymerization reactions, however when two or three of these cyclics are mixed together they have much lower melting points (around 300 °C). Therefore, ring-openg polymerization can be easily carried out around 350 °C. The details of the ring-opening polymerization will be described in later sections.

9.3.2. Synthesis and characterization of cyclic(arylene ether phthalazine) oligomers.



9.5

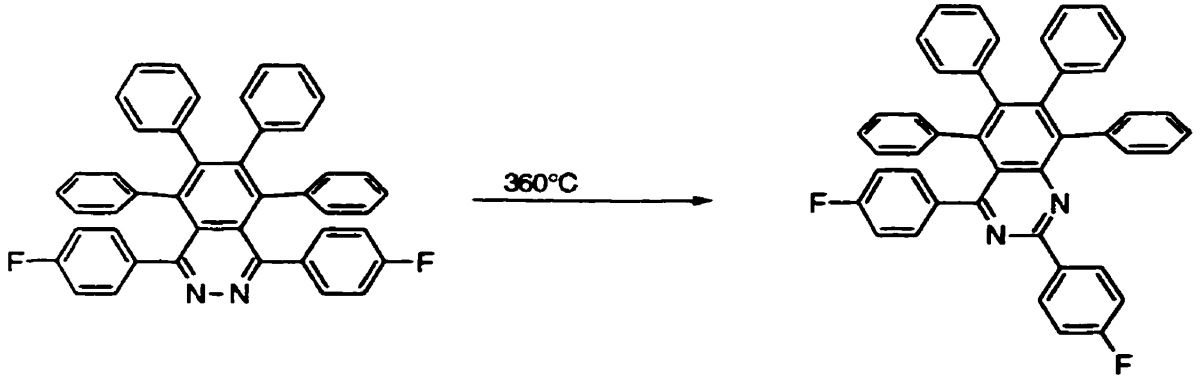


Scheme 9.2. Conversion of cyclic(ether ketone)s into cyclic(ether phthalazine)s.

The cyclic(ether ketone)s have also been transformed into cyclic(ether phthalazine)s which, in the corresponding linear polymers, have higher T_gs than the cyclic(ether ketone)s.[14] The reaction is shown in Scheme 9.2. The completion of the

reactions was confirmed by ^{13}C-NMR studies. The ^{13}C peak of the carbonyl group in the starting cyclic was below the detection limit. MALDI-TOF-MS analyses of these cyclic(ether phthalazine)s are quite different from the cyclic(ether ketone)s. The addition of a silver salt does not improve the analysis sensitivity and quality. All of the MS analyses can be carried out without the assistance of silver in the presence of dithranol as matrix and the results are in agreement with calculated results (Table 9.3). Samples analyzed in the presence of silver give the same results.

Model reactions on phthalazines have previously indicated that both rearrangement and cross-linking reactions occurred on heating.[23] The rearrangement reaction on phthalazine **9.6** forms a quinazoline **9.7** (Scheme 9.3), however, the nature of the cross-linking reaction is unclear. DSC studies have shown that in this class of cyclics some exothermic reactions take place when heated higher than 300 °C. As expected, the DSC scan of **9.5b** shows similar behavior. Generally, these reactions take place around 330 °C (Table 9.4). These reactions precluded further work on the ring-opening polymerization of these cyclics because melting points of this class of cyclics are higher than 330 °C and polymerization has to be carried out above the melting points which would be above the decomposition temperature.



9.6 **9.7**

Scheme 9.3. Rearrangement reaction of a phthalazine

Table 9.3. MALDI-TOF-MS analyses of cyclic(ether phthalazine)s (g/mol).

		M2	M3	M4	M5	M6	M7	M8
	Meas.	1621	2432.1	3244.7	4056.1	4868.6	5676.5	6490.5
9.5a	Calc.	1622	2433	3244	4055	4866	5677	6488
	Intensity	74.5	100	87	45	16	4	0.5
	Meas.	1539.1	2305.6	3076.4	3846	4616.4	5385.4	6149.7
9.5b	Calc.	1538	2306	3075	3844	4613	5382	6151
	Intensity	85	100	41	50	30	12	3
	Meas.	1671.4*	2516.8*	3356.9*	4197.7*	5036*	5874.6*	6714.6*
9.5c	Calc.	1686	2529	3372	4214	5058	5901	6744
	Intensity	65	71	100	59	20	6	2
	Meas.	1782.1	2675.2	3567.9	4458.7	5352		
9.5e	Calc.	1782	2673	3564	4455	5346		
	Intensity	100	24	17	6	0.5		
	Meas.	1865.8	2800.8	3735.6	4671.8	5602.3	6537.1	7481.4
9.5f	Calc.	1867	2801	3735	4669	5602	6536	7470
	Intensity	95	100	71	27	8	2	0.3
	Meas.	1386.8	2077.7	2771.1	3465.6	4159.4	4852.2	5545.5
9.5g	Calc.	1386	2078	2771	3464	4157	4849	5542
	Intensity	32	100	83	92	62	10	5
	Meas.	1665.2	2449.8	3355.7	4188.8	5024.6	5860.4	
9.5h	Calc.	1666	2499	3332	4165	4997	5830	
	Intensity	100	47	41	24	6	0.3	

* Molecular peak corresponding to loss of one methyl group.

Table 9.4. Properties of cyclic(ether phthalazine)s

Cyclics	T_R(°C) [a]	TGA (°C) [b]
9.5a	330	520
9.5b	342	550
9.5c	307	480
9.5d	332	518
9.5e	331	453
9.5f	358	543
9.5g	343	530
9.5h	319	494

a. Peak temperature of the exothermic reaction. Detected by DSC under N_2 atmosphere, heating rate was 20 °C/min.

b. Temperature at which 5% weight loss was reported. Measured under N_2 atmosphere, heating rate was 20 °C/min.

9.3.3. Ring-opening polymerization of cyclic(ether ketone)s containing the tetraphenylbenzene moiety.

As we can see from previous sections, cyclic oligomers containing the tetraphenylbenzene moiety have extremely high melting points which makes them unsuitable for a normal ring-opening polymerization reaction, since the melt ring opening-polymerization has to be carried out above the melting points of the oligomers. This problem has also been encounted in other cyclic systems and synthesis of co-cyclics has proved insufficent to solve the problem[1]. Herein, we describe a new strategy to lower the melting points of cyclic oligomers to allow the ring-opening polymerization to be carried out at much lower temperatures. The ring-opening polymerization of cyclic(ether ketone) oligomers containing a thio-ether linkage can be initiated by elemental sulfur or a disulfide compound. In 1989, Cella *et.al.*[1] demonstrated that thio-ether imide co-cyclics underwent ring-opening polymerization in the presence of Na_2S in the melt, presumably via an anionic mechanism. Most recently,

we reported the free radical ring-opening polymerization of some cyclic oligomers containing a thio-ether linkage[24,25]. In a typical example, cyclic(phenylene sulfide) oligomers prepared from *p*-bromothiophenol underwent a free radical ring-opening polymerization to form high molecular weight PPS. In this research, we have used diphenyl disulfide as the initiator to demonstrate the ring-opening polymerization on blends of the cyclic oligomers.

The cyclic(ether ketone) oligomers containing the diphenylbenzene moiety (**9.8**) were synthesized by the previously reported procedure in which the reactants were delivered by a syringe pump.[13] Cyclic(ether ketone) **9.3i** contains 32% of dimer (n = 2), 20% of trimer (n = 3), 11% of tetramer (n = 4) and small amounts of higher oligomers, while cyclic(ether ketone) **9.8** consisted of 16% dimer, 15% trimer, 8% tetramer and other higher oligomers as determined by gradient HPLC. From GPC, cyclic **9.3i** has a number average molecular weight of 2380 (M_w = 4770) and cyclic **9.8** has a number average molecular weight of 2103 (M_w = 8247).

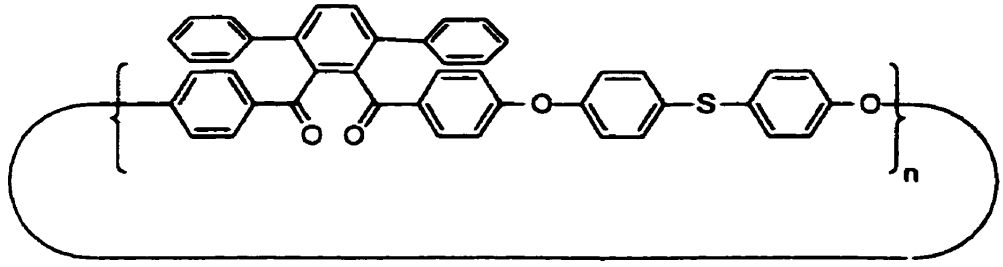
Table 9.5. Melting points of cyclic mixtures

weight ratio **9.3i** : **9.8**	melting points (°C)*
8:2	250, 380
7:3	250,360
6:4	250
5:5	250,360
4:6	360
2:8	380

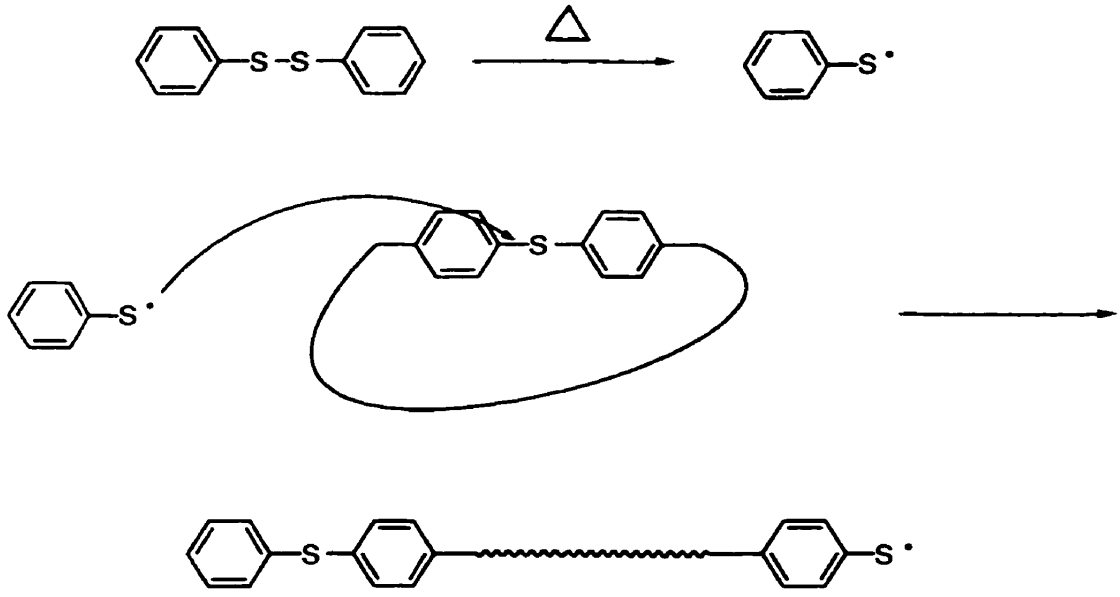
* Peak temperature obtained from DSC.

DSC analysis showed both of the cyclic oligomers have very high melting points around 390 °C. The high melting points are due to the high concentrations of cyclic dimers and trimers, which make it difficult to carry out a ring-opening polymerization reaction in the melt since the melt ring-opening polymerization has to be done above the melting points. If different cyclic oligomers are blended together, the

melting point would be expected to be significantly lower. To test this, blends consisting of different ratios of cyclics **9.3i** and **9.8** were prepared from chloroform solution, dried and subjected to DSC analysis. The DSC scans indicated that the blend with weight ratio of **9.3i** and **9.8** equals to 6:4 has the lowest melting point, 250 ℃ (peak temperature, Table 9.5). This suggested that using the mixture this melt ring-opening polymerization reaction could be carried out at a much lower temperature.



9.8



Scheme 9.4. Free-radical initiated ring-opening polymerization

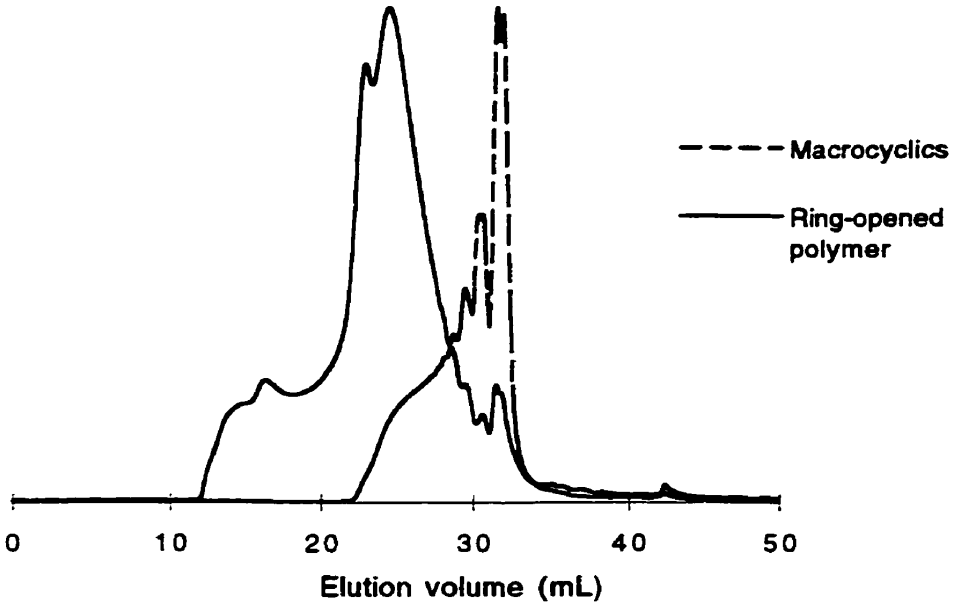


Figure 9.7. A GPC comparison of a cyclic mixtures before and after ring-opening polymerization

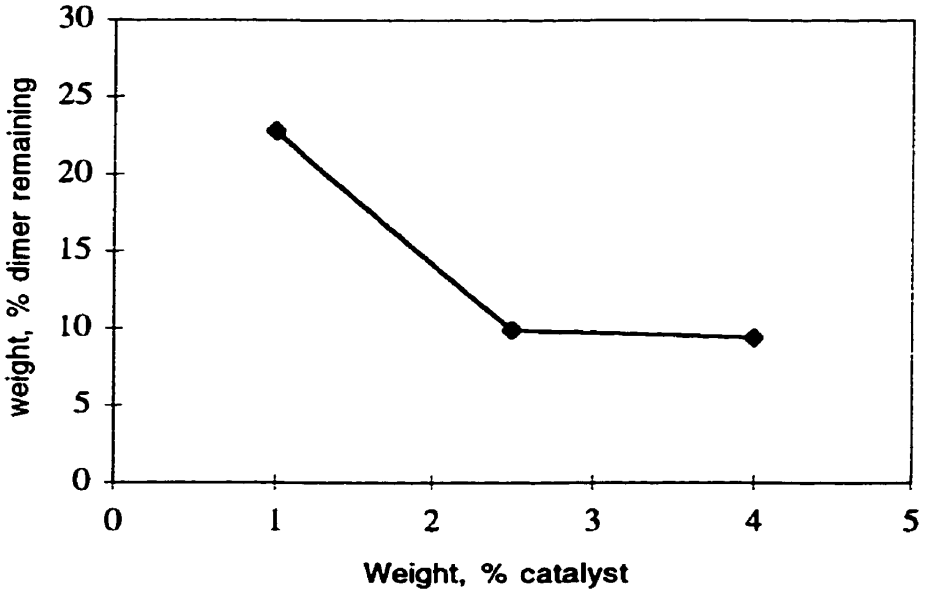


Figure 9.8. Effect of catalyst amount on ring-opening polymerization (350 °C, 15 min)

The cyclics **9.3i**, **9.8** and initiator were mixed together by dissolving them in chloroform, evaporating off the solvent and drying at 100 °C under vacuum for 24 hours. The mixture was charged into a Pyrex 10 mL test tube equipped with a nitrogen inlet and placed in a salt bath to carry out the ring-opening polymerization. The resulting solids were subjected to GPC and DSC analysis. The effects of catalyst amount, temperature and time on the ring-opening polymerization were studied. The efficiency of the ring-opening polymerization was determined by calculating the percentage of dimer remaining and the amount of products insoluble in chloroform. The ring-opening polymerization reaction is shown in Scheme 9.4. Figure 9.7 shows an example of GPC results on a cyclic oligomer mixture before and after the ring-opening polymerization.

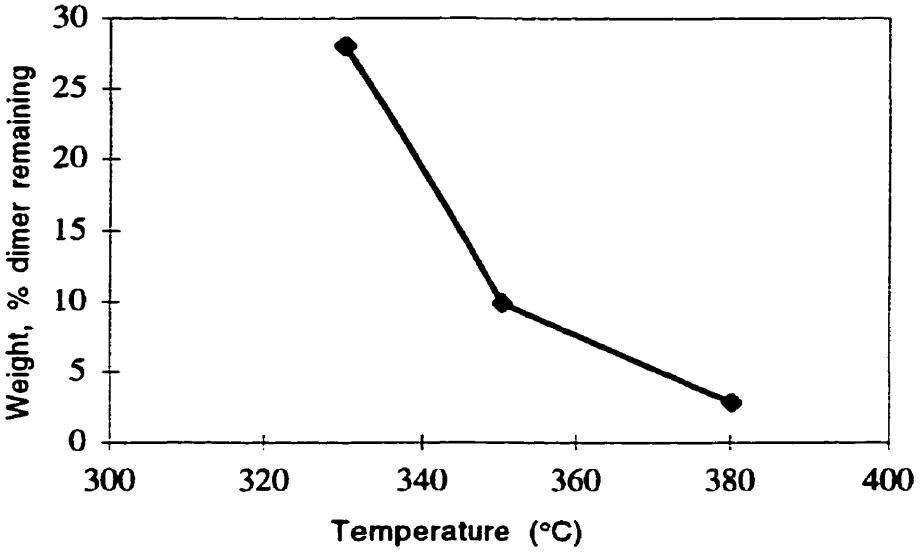


Figure 9.9. Effect of temperature on the ring-opening polymerization (2.5 % PhSSPh, 15 min)

The effects of catalyst amount, temperature, and time on the melt ring-opening polymerization are shown in Figure 9.8, Figure 9.9, and Figure 9.10, respectively. As the amount of diphenyl disulfide increases, the conversion of the ring-opening reaction increases, however the effect of the initiator is not very significant when the weight percentage exceeded 2.5% (Figure 9.8). At 300 °C, the products were quite soluble in chloroform, however the ring-opening polymerization did not go to completion. At 380 °C, the conversion was complete, but most of the products were insoluble in chloroform. At 350 °C, the ring-opening reaction went almost to

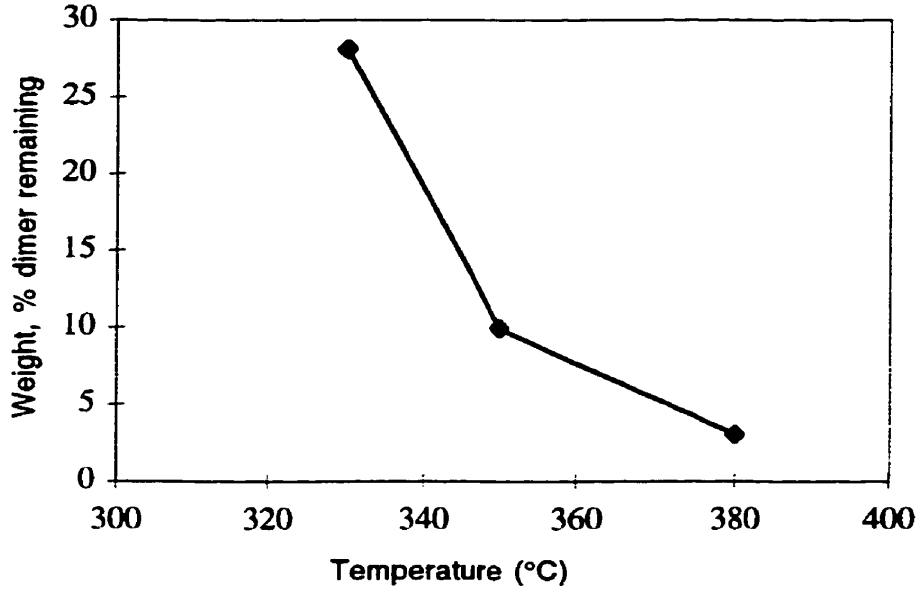


Figure 9.10. Effect of time on the ring-opening polymerization (2.5 % PhSSPh, 350 °C)

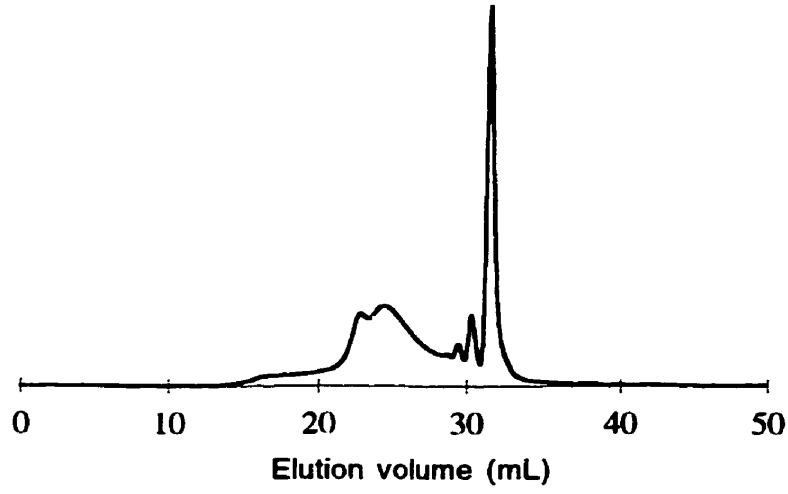


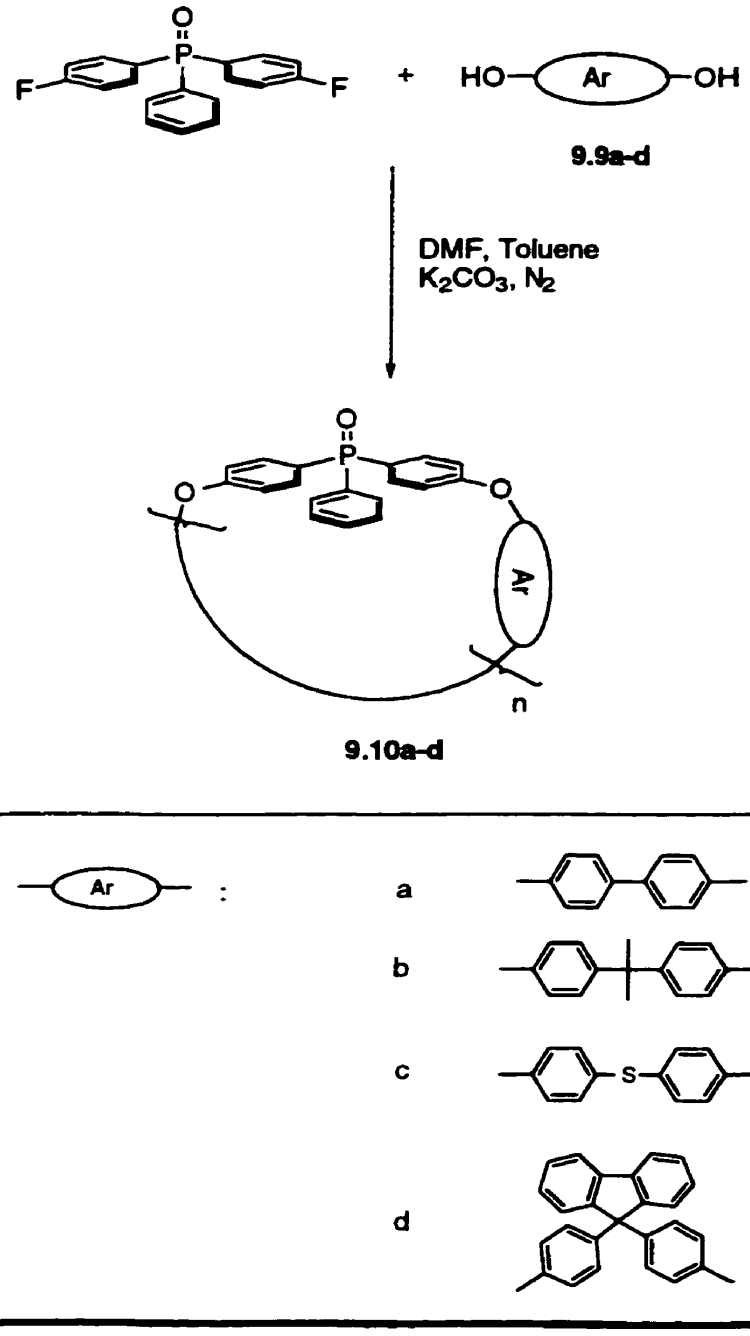
Figure 9.11. GPC chart of reaction products of cyclic oligomers **9.3i** at 380 °C (2.5 % PhSSPh, 15 min)

completion and gave soluble products. Conversion also increased with reaction time, however, longer times tended to give more insoluble products. After 20 min of reaction time at 350 °C small amounts of insoluble products were formed. The soluble polymer formed had M_n of 15200 and M_w of 240,000 from GPC. A DSC scan shows that the polymer formed has a T_g of 218 °C, which is comparable with the theoretic T_g for this polymer of 221 °C. The temperature of 5% of weight loss of this polymer in nitrogen is 496 °C. In contrast in the polymerization of cyclic oligomers **9.3i** alone, with 2.5% weight percentage of the initiator at 380 °C for 15 min, large amount of low molecular weight cyclics remained (Figure 9.11). Without adding diphenyl disulfide, the cyclic blend did not give any indication of ring-opening polymerization at 350 °C even for 1 h. All of these studies confirmed that diphenyl disulfide is a very efficient catalyst for the ring-opening polymerization of cyclic(ether ketone) oligomers containing a thio-ether linkage. By blending of cyclics **9.3i** and **9.8**, ring-opening polymerization can be carried out at 350 °C very efficiently to obtain linear high T_g polymer.

9.4. Cyclic(arylene ether) oligomers containing the phenylphosphine oxide moiety.

9.4.1. Synthesis of cyclic(arylene ether) oligomers containing the phenylphosphine oxide moiety.

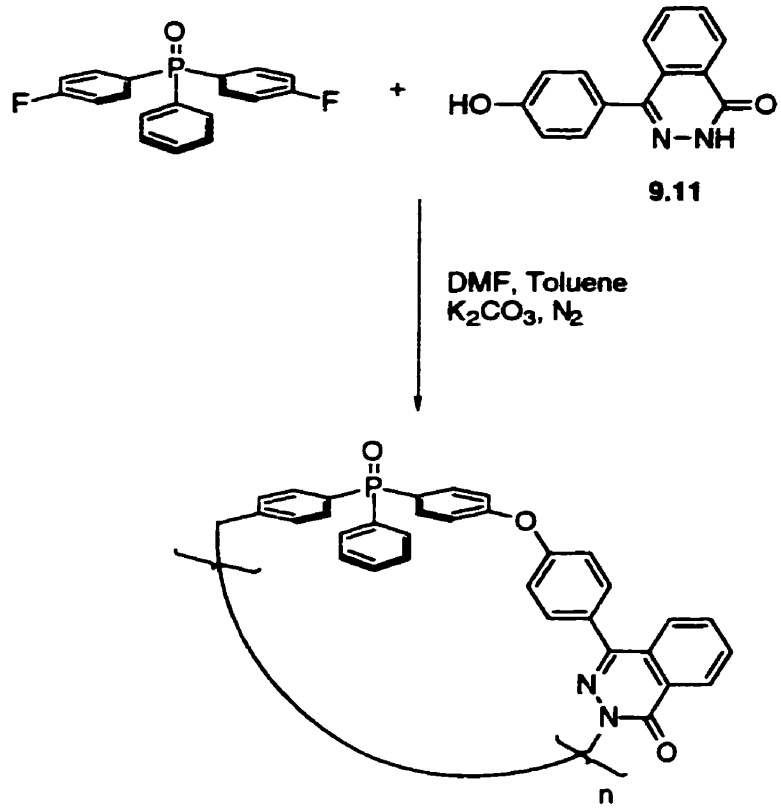
The preparation of cyclic(arylene ether) oligomers containing the phenyl phosphine oxide moiety was carried out under high dilution conditions in DMF as developed in this laboratory. Several dihydroxy compounds, **9.9a-d**, as well as 1,2-dihydro-4-(4-hydroxyphenyl) (2*H*) phthalazin-1-one (**9.11**), were chosen to synthesize the cyclic(arylene ether) oligomers by reacting with bis(4-fluorophenyl)phenylphosphine oxide, a monomer that has been extensively used to prepare high performance polymers.[15-20] The cyclization reactions are schematically shown in Schemes 9.5 and 9.6, respectively.



Scheme 9.5. Synthesis of cyclic(arylene ether) oligomers containing the phenylphosphine oxide moiety.

The linear polymer derived from bis(4-fluorophenyl)phenylphosphine oxide and **9.11** has been found to have a very high glass transition temperature (T_g = 309 °C)

and very high thermal stability ($T_{d\text{-}5\%}$ = 512 °C, N_2).[26] The synthesis of cyclic(arylene ether) oligomers **9.12** was achieved by two types of nucleophilic substitution reaction. One is the normal phenoxide anion substitution, while the another one is a novel N-C coupling reaction.[26-29] Some cyclic and cocyclic oligomers derived from **9.11** have been previously synthesized and characterized.[30]



9.11

9.12

Scheme 9.6. Synthesis of cyclic(arylene ether) oligomers from 1,2-dihydro-4-(4-hydroxyphenyl) (2*H*) phthalazin-1-one.

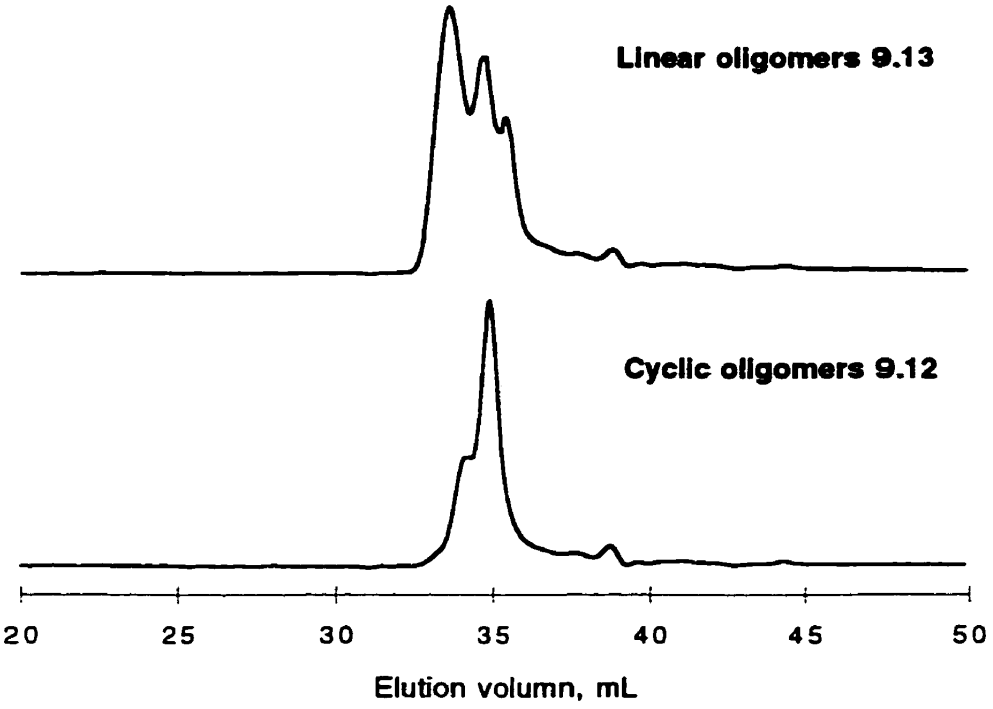


Figure 9.12. GPC traces of cyclic oligomers **9.12** and linear oligomers **9.13**

Table 9.6. GPC analyses of cyclic(arylene ether) oligomers containing the phenylphosphine oxide moiety*

Cyclic oligomers	M_n (g/mol)	M_w (g/mol)
9.10a	1000	1130
9.10b	1210	1440
9.10c	1230	1520
9.10d	1350	1590
9.12	840	890

* Measured by GPC and calibrated with polystyrene standards. THF with 0.5 % LiBr (w/v) was the eluent and the flow rate was 1.0 mL/min.

All the cyclic oligomers were obtained in almost quantitative yields. They have very good solubilities in common organic solvents, such as $CHCl_3$, THF, DMF, DMAc. Despite their good solubilities, attempts to analyze the cyclic products was unsucessful by GPC with chloroform as eluent due to the presence of the phosphine oxide moiety in the cyclic oligomers. Analysis by gradient HPLC with THF and water as eluents was also unsuccessful. These two techniques have been routinely used in the analysis of cyclic oligomers. When THF with 0.5 % LiBr (w/v) added was used as the eluent, the cyclic oligomers can be analyzed by GPC. The apparent molecular weights of these cyclic oligomers determined by GPC are shown in Table 9.6 and the GPC chart of cyclic oligomers **9.12** is shown in Figure 9.12. For comparison, the GPC chart of linear oligomers **9.13** is also shown in Figure 9.12.

9.4.2. Cyclic nature of the cyclic(arylene ether) oligomers.

Gradient HPLC analysis can not be used for the present cyclic systems. However, matrix assisted laser desorption mass spectroscopy has been demonstrated in this laboratory to be a powerful tool to analyze cyclic oligomers.[12,31,32] By using 1,8,9-anthracenetriol (dithranol) as the matrix, all the cyclic oligomeric samples gave the correct molecular ion signals for the cyclic systems. Cationic agents, such as a silver or a lithium salt, are not required for these cyclic systems. Very high signal/noise ratios were obtained in every case and repeating units up to 12 have been detected. A typical MALDI-TOF-MS spectrum is shown in Figure 9.13, which was obtained for cyclic sample **9.12**. Other data from MALDI-TOF-MS analyses are given in Table 9.7. The relative intensities for molecular peaks given in the table do not represent the actual compositions of the cyclic oligomers. Gradient HPLC has been used to determine the compositions of other cyclic systems.[12,31] However, this technique failed for the present cyclic system due to the presence of the phosphine oxide moiety. No signal could be detected in our gradient HPLC system, although many different conditions were used.

Table 9.7. MALDI-TOF-MS analysis results for cyclic(arylene ether) oligomers containing the phenylphosphine oxide moiety (g/mol).

Cyclics		M_2^+	M_3^+	M_4^+	M_5^+	M_6^+	M_7^+	M_8^+	M_9^+	M_{10}^+	M_{11}^+	M_{12}^+
	measd	921	1381	1481	2301	2761	3222	3682	4142	4603	5063	
9.10a	calcd	920	1380	1841	2301	2761	3221	3681	4141	4601	5062	
	intensity	100	47	46	24	15	8	4	2	1	1	
	measd	1005	1508	2011	2513	3016	3518	4021	4523	5026	5528	6031
9.10b	calcd	1004	1507	2009	2511	3013	3515	4018	4520	5022	5524	6026
	intensity	100	67	42	28	17	10	5	3	2	1	1
	measd	985	1478	1970	2463	2956	3448	3941	4434	4925		
9.10c	calcd	984	1476	1968	2461	2953	3445	3937	4429	4921		
	intensity	100	41	20	12	7	4	2	1	1		
	measd	1251	1876	2502	3129	3755	4381	5006	5631	6255		
9.10d	calcd	1248	1873	2497	3121	3745	4369	4994	5618	6242		
	intensity	100	40	23	15	10	5	3	2	1		
	measd	1024	1536	2048	2560	3072	3583	4096	4607	5120	5635	6148
9.12	calcd	1024	1536	2049	2561	3073	3585	4097	4609	5121	5634	6146
	intensity	100	52	45	30	23	15	10	6	4	2	1

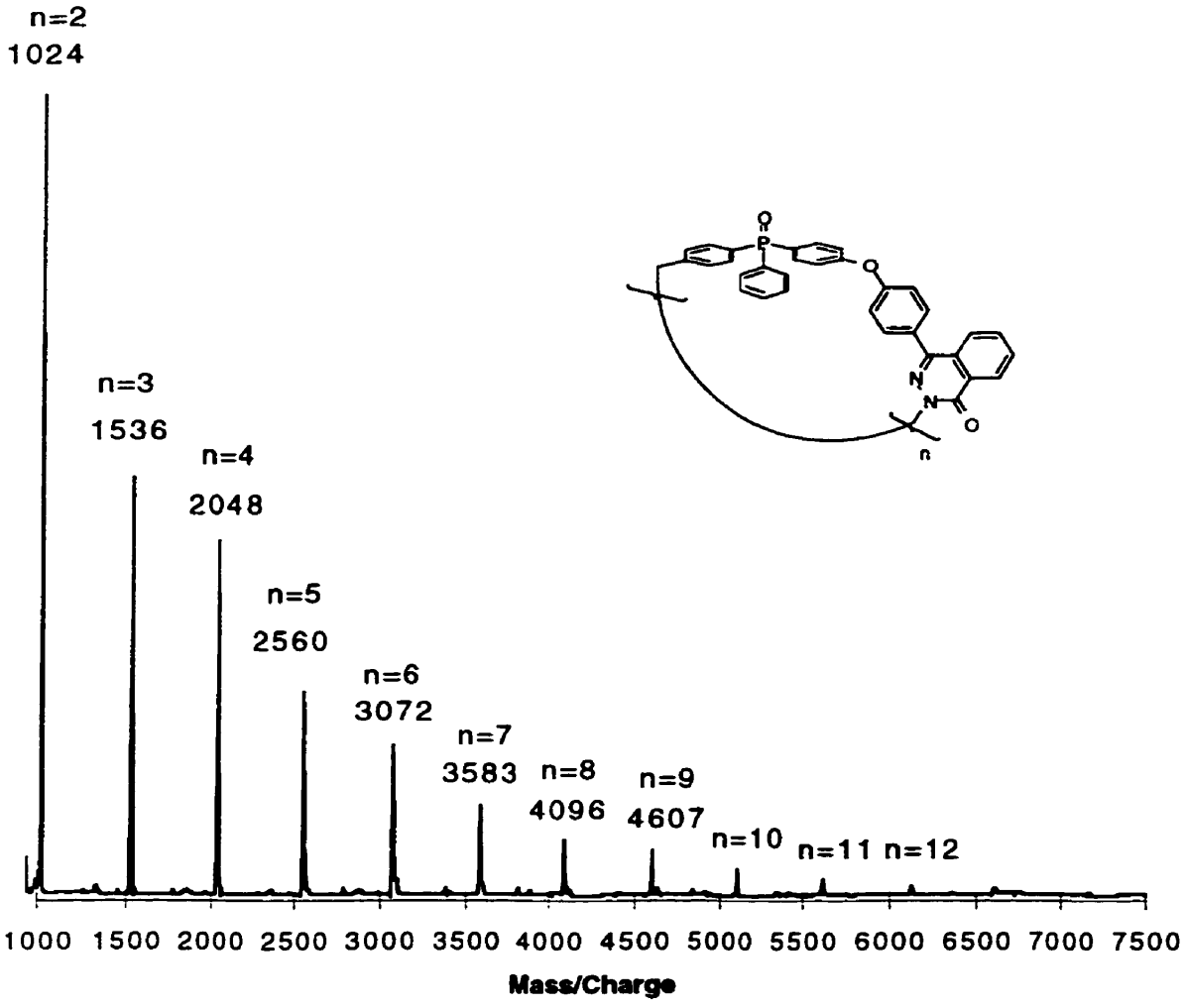
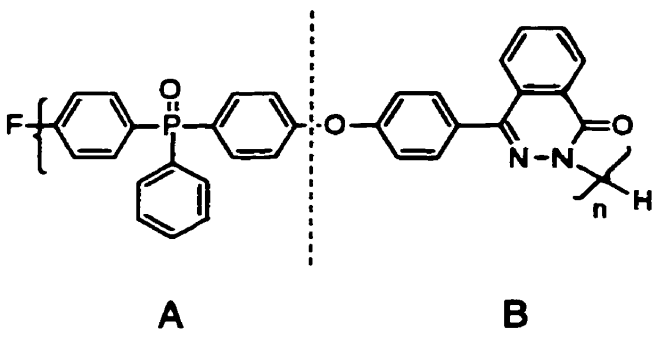


Figure 9.13. MALDI-TOF-MS spectrum of cyclic oligomers **9.12**



9.13

From Figure 9.13, one can see that there are no linear oligomers and no fragmentation was detected, which indicates that the low molecular weight oligomers consist of essentially pure cyclic oligomers. To demonstrate that the MALDI-TOF-MS technique can detect the presence of linear oligomers, an authentic linear oligomeric sample **9.13**, along with a cyclic oligomeric sample **9.12'** containing linear oligomers by deliberately adding 5 % excess of reactant **9.11**, was synthesized and analyzed by MALDI-TOF-MS. The linear oligomeric sample **9.13** has a weight average molecular weight of 1070 g/mol and a number average molecular weight of 970 g/mol as determined by GPC using polystyrene standards. The MALDI-TOF-MS spectra for both of the samples (Figure 9.14-15) showed clearly the presence of linear oligomers. In Figure 9.14, three types of linear oligomers were detected as expected theoretically, with fluorine end groups $(\mathbf{AB})_n\mathbf{A}$, phthalazinone end groups $\mathbf{B}(\mathbf{AB})_n$, and one fluorine and one phthalazinone end group $(\mathbf{AB})_n$. The MALDI-TOF-MS spectrum showed in Figure 9.15 was obtained for the cyclic oligomer sample **9.12'** prepared by using 5% excess of reactant **9.11**. In the mass spectrum, peaks corresponding to both cyclic oligomers and phthalazinone ends linear oligomers are clearly showed. This indicates that the presence of a very small amount of linear oligomers due to the slightly imbalance of starting materials can be detected by MALDI-TOF-MS technique.

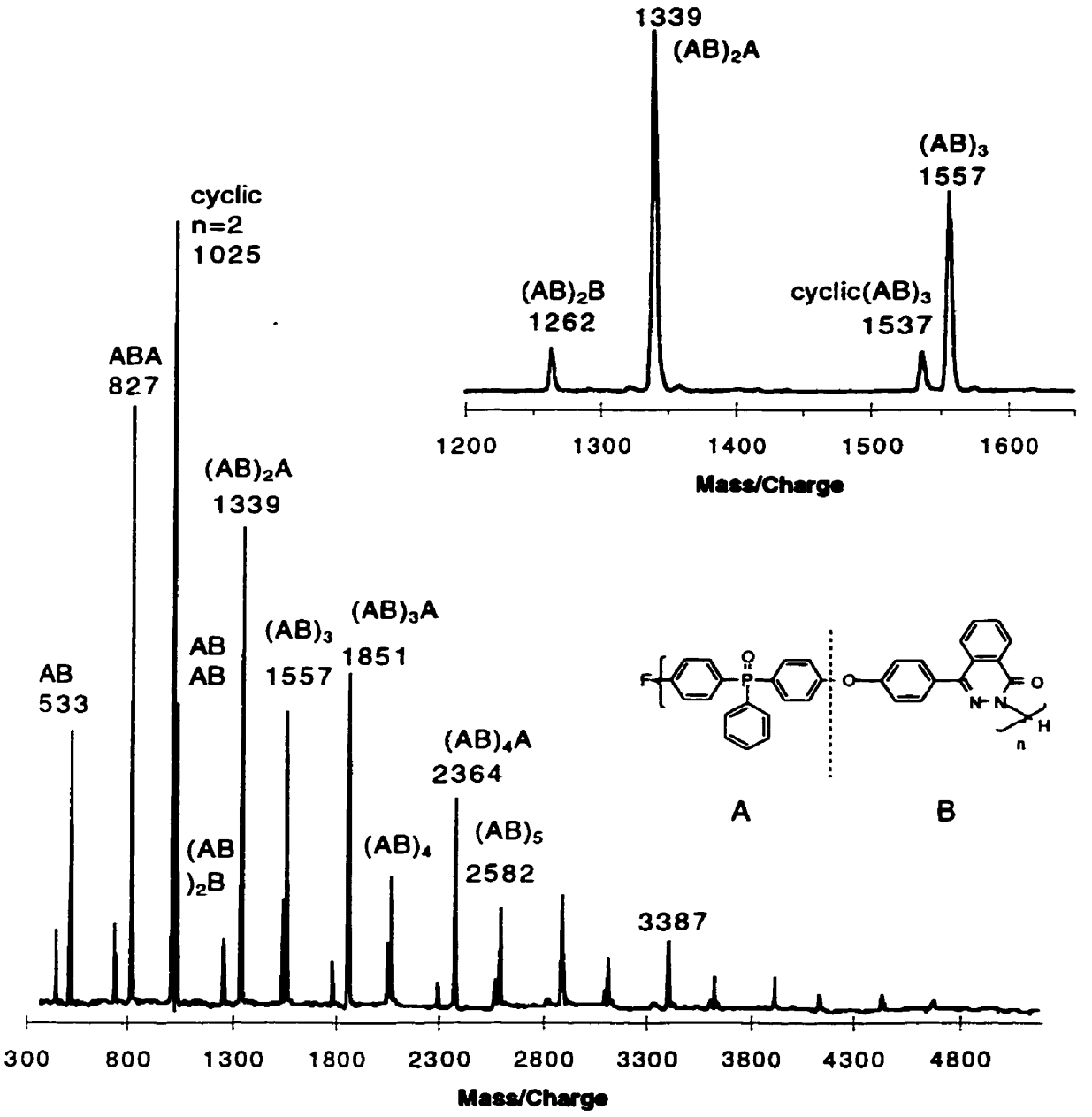


Figure 9.14. MALDI-TOF-MS spectrum of linear oligomers **9.13** along with an inset of the spectrum.

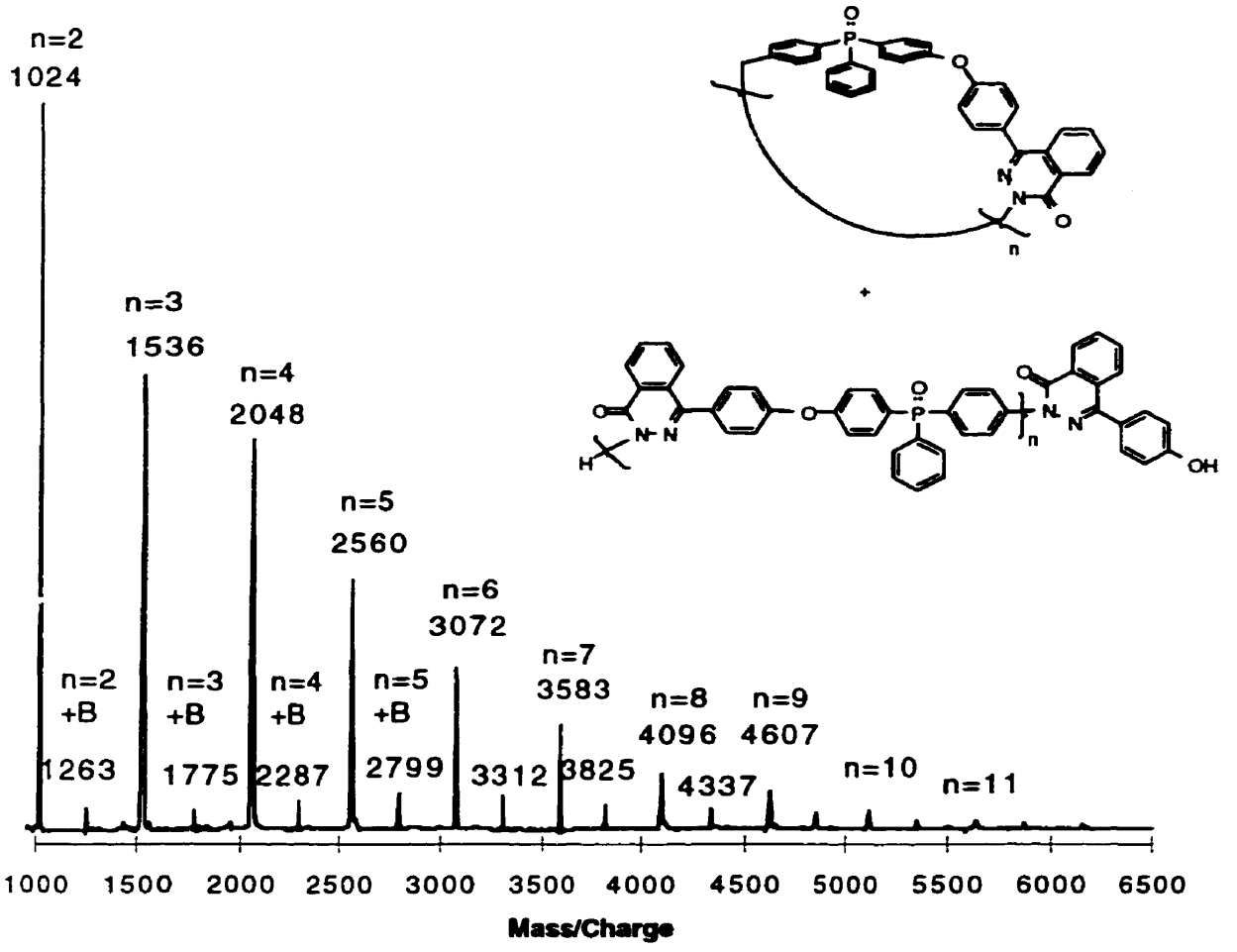


Figure 9.15. MALDI-TOF-MS spectrum of the cyclic sample **9.12'** prepared in the presence of excess of monomers **9.11**.

9.4.3. Thermal properties of the cyclic(arylene ether) oligomers.

For a melt ring-opening polymerization reaction to be successful, high crystallinity and high melting points in the cyclic oligomers should be avoided, since the ring-opening polymerization has to be carried out above the melting point. The cyclic(arylene ether) oligomers containing the phenyl phosphine oxide moiety do not show any indication of melting points based on the DSC analyses. This indicates that these cyclic oligomers are amorphous which should facilitate the ring-opening polymerization reaction. The thermal properties of these cyclic oligomers are listed in Table 9.8. All of the T_gs are below 300 °C. Cyclic oligomers **9.10d** has the highest T_g, 276 °C, among this series of cyclic oligomers, while the cyclic oligomers **9.10c** has the lowest T_g, 167 °C. In addition, they have very high thermal stabilities as indicated by their 5 % weight losses determined by TGA.

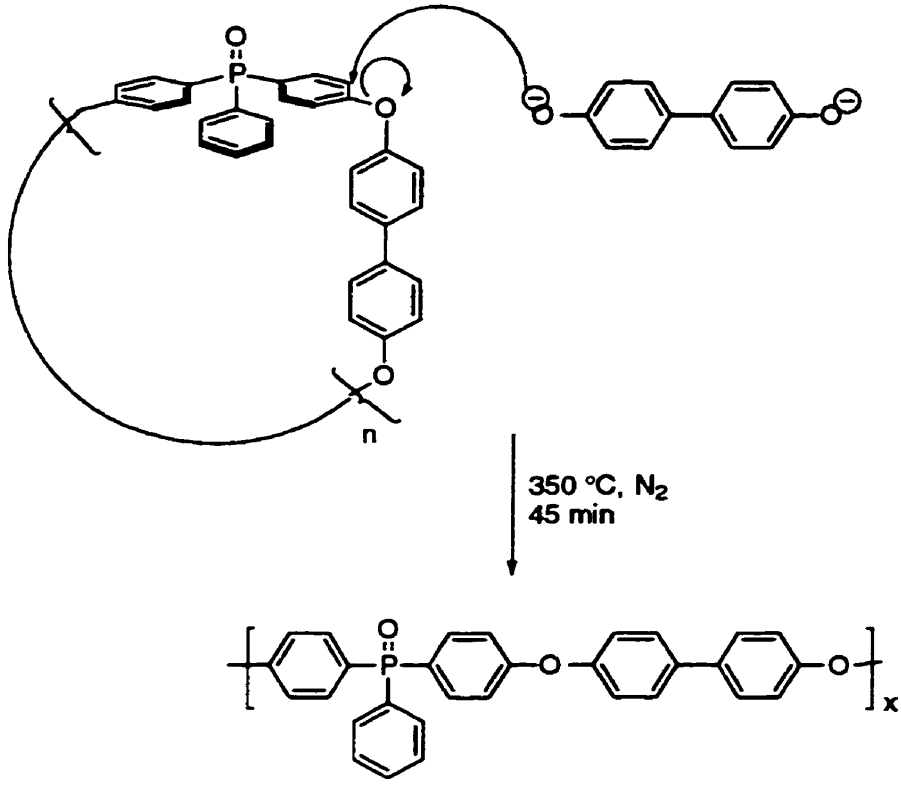
Table 9.8. Thermal properties of cyclic(arylene ether) oligomers containing the phenylphosphine oxide moiety.

Cyclic oligomers	T_g(°C) [a]	TGA(°C) [b]
9.10a	239	563
9.10b	201	519
9.10c	167	465
9.10d	276	477
9.12	273	506

a. Obtained by DSC under nitrogen atmosphere with heating rate of 20 °C.

b. 5 % weight loss temperature.

9.4.4. Ring-opening polymerization of the cyclic(arylene ether) oligomers.



Scheme 9.7. Melt ring-opening polymerization of cyclic oligomers **9.10a** in the presence of an anionic initiator.

A melt ring-opening polymerization of cyclic oligomers **9.10a** was carried out at 350 °C for 45 min by using 1 mol% of potassium biphenoxide as the anionic initiator. The polymerization reaction is depicted in Scheme 9.7. The using of potassium biphenoxide as an anionic initiator has been studied in detail for ring-opening polymerization of cyclic(arylene ether ketone) oligomers.[33] The starting cyclic oligomers **9.10a** has an inherent viscosity of 0.16 dL/g and is soluble in THF at room temperature. After the ring-opening polymerization reaction, the resulting material is not soluble in THF, but it is readily soluble in $CHCl_3$. GPC results are not available because of the strong interaction between the polymer and the column when $CHCl_3$ is used as the eluent. The inherent viscosity of the resulting polymer is 0.48 dL/g, which indicates the formation of high molecular weight polymer. The T_g of the resulting

polymer is 245 °C, which is the same value as that obtained from a conventional condensation polymerization reaction.[16]

9.5. Conclusions

A new series of macrocyclic(ether ketone)s containing the tetraphenylbenzene moiety has been synthesized by a high-dilution method. To overcome the problem of solubility of the diketone reactant, the reactants were added in solid form over a period of several hours. This synthetic strategy gave high yields of macrocyclic(ether ketone)s consisting principally of dimer, trimer and tetramer. This series of cyclics show high thermal stabilities and they have high T_gs. The macrocyclic oligomers have extremely high melting points, however, by the use of mixtures of cyclics the T_ms are significantly lowered to make them suitable precursors for ring opening polymerization to give high performance polymers. Cyclic(ether ketone)s were also transformed into (ether phthalazine)s which undergo exothermic reactions around 330 °C which precludes their use in ring-opening polymerization reactions.

Cyclic(arylene ether) oligomers containing the phenylphosphine oxide group have been synthesized from bis(4-fluorophenyl)phenylphosphine oxide and dihydroxy compounds **9.10a-d**, as well as the phthalazinone monomer **9.11**. All of these cyclic oligomers are amorphous with T_gs below 280 °C. The cyclic oligomers were analyzed by NMR, GPC, and MALDI-TOF-MS techniques. In the presence of an anionic initiator, the cyclic oligomers readily undergo ring-opening polymerization reaction in the melt, affording high molecular weight polymers.

9.6. Experimental section

Materials

1,2-bis(4-fluorobenzoyl)-3,4,5,6-tetraphenylbenzene (**9.1**) was syntheized according to the previously reported method.[11] Bis(4-fluorophenyl)phenylphosphine oxide was prepared by a Grignard technique[17] and recrystallized from toluene/hexane (v : v = 1 : 3). 1,2-Dihydro-4-(4-hydroxyphenyl) (*2H*) phthalazin-1-one was synthesized according to the previously reported method.[27,28] **9.2a**, **9.2b**, and **9.2f** were supplied by General Electric Co. **9.2d**, **9.2g**, **9.2h** and **9.2i** were purchased from Aldrich Chemical Co. and purified by recrystallization. Diphenyl disulfide was

supplied by Lancaster and purified by recrystallization from ethanol (m.p. 60-61 °C). All solvents were used directly as obtained without further purification.

Measurements

GPC analyses were performed on a Waters 510 HPLC equipped with 5μ phenogel columns (linear, 3x500 Å) arranged in series and UV detector. Chloroform was used as the eluent for the analysis of cyclic(arylene ether) oligomers containing the tetraphenylbenzene moiety, while HPLC grade tetrahydrofuran (THF) containing 0.5 % w/v LiBr was used as the eluent for the analysis of cyclic(arylene ether) oligomers containing the phenylphosphine oxide moiety. DSC scans were obtained using a Seiko 220 DSC instrument at a heating rate of 20 °C/min in N_2 (160 mL/min). The weight loss data were obtained from a Seiko 220 TG/TGA instrument at a heating rate of 20 °C/min in nitrogen. Gradient HPLCs were performed on a Milton Roy CM4000 multiple solvent delivery system with a C8 Prime Sphere 4.6x250 mm column, THF and water as eluent solvent, and a UV detector at 300 nm. All samples were stirred on a mechanical shaker until dissolved into solutions before analyses. NMR spetra were recorded on a Varian Unity 500 (500 Mhz) and $CDCl_3$ was used as solvent. TMS was used as reference for ^{1}H-NMR and computer reference was used directly for ^{19}F-NMR. For easy identification, fluorobenzene was added. Inherent viscosities were measured in $CHCl_3$ (0.5g/dL) at 25.0 ± 0.1 °C using an Ubbelohde viscometer.

MALDI-TOF-MS analysis for the cyclic samples.

Matrix assisted laser desorption ionization - time of flight - mass spectroscopy (MALDI-TOF-MS) analysis was performed on a KOMPACT-MALDI-TOF-MS.

The analysis solution was prepared from 20 μL of cyclic sample solution, 20 μL of silver trifluoroacetate solution and 100 μL of Dithranol solution (matrix). The cyclic sample solution was prepared from 5 mg of sample and 1 mL chloroform. The matrix solution consisted of 10 mg of dithranol and 1 mL chloroform. The concentration of silver trifluoroacetate was 5 mg/mL. The sample solution (0.2 μL) was spotted on the sample slot and subjected to analysis. The laser power was set at 95.

General procedure to prepare cyclic(ether ketone) oligomers containing the tetraphenylbenzene moiety.

A 1000 mL three neck round bottom flask equipped with a Dean-Stark trap and a nitrogen inlet was charged with 500 mL of DMF, 25 g of anhydrous potassium carbonate and 40 mL of toluene. The mixture was refluxed for 1 h to remove water, then 5.0 g of 1,2-bis(4-fluorobenzoyl)-3,4,5,6-tetraphenylbenzene (**9.1**) and an equivalent amount of bisphenol were added in 10 portions directly to the flask in solid form over 9 h. The resulting mixture was kept at reflux for another 10 h to and cooled down. After filtration, the solvents were removed on a rotary evaporator under vacuum. The resulting solid was dissolved in 250 mL chloroform and refiltered. The solution was concentrated under vacuum in a rotary evaporator to 50 mL and precipitated out by addition to methanol. The resulting solid was dried at 100 °C for 24 h under vacuum. All the cyclic oligomers were obtained as white powders.

Preparation of linear oligomers of 9.4.

A 25 mL three neck round bottom flask equipped with a Dean-Stark trap and a nitrogen inlet was charged with 1.500 g (2.4 mmol) of **9.1**, 0.547 g (2.4 mmol) of **9.2a**, 3.0 g of anhydrous potassium carbonate, 8.0 mL of DMF and 6.0 mL of toluene. The mixture was placed in a preheated oil bath and kept at reflux for 1 h. After cooling down, the reaction mixture was filtered into a methanol-glacial acid solution to precipitate out the products. The solid products were dissolved in 20 mL chloroform and filtered through a thin layer of Celite. The chloroform solution was condensed and poured into 100 mL of methanol. The white linear oligomers were obtained by filtration and dried at 100 °C under vacuum for 24 h. Yield: 1.46 g (71%).

General procedure for the preparation of cyclic(ether phthalazine)s.

To a cooled solution of 0.8 g of the above cyclic(ether ketone) in dioxane (12 mL) and concentrated hydrochloric acid (2 mL) was added hydrazine monohydrate (8 mL) over a period of 15 min. The reaction mixture was refluxed for 8 h, cooled down and poured into 25 mL of water. The light yellow solid was washed several times with methanol and dried at 100 °C for 24 h under vacuum.

Free radical initiated ring-opening polymerization.

A mixture of cyclic(ether ketone) oligomers (0.2 g) and the disulfide initiator were dissolved in 5 mL chloroform and then the solvent was evaporated. The resulting solids were dried at 100 °C under vacuum for 24 h. The mixture was charged into a 10 mL Pyrex test tube equipped with a nitrogen inlet and heated in a salt bath. The resulting amber colored solid was subjected to GPC and DSC analysis.

Synthesis of cyclic(arylene ether) oligomers from bis(4-fluorophenyl)phenylphosphine oxide.

A typical example is given as follows. A 500 mL flask equipped with a Dean-Stark trap and condenser, and a nitrogen inlet was charged with 250 mL of DMF, 20 mL of toluene and 25.0 g of anhydrous K_2CO_3. The mixture was heated to reflux with stirring. Then the solution of bis(4-fluorophenyl)phenylphosphine oxide (3.1427 g, 0.01 mol) and **9.11** (2.3825g, 0.01 mol) in 100 mL of DMF was delivered to the reaction flask over a period of 8 h *via* a syringe pump. After the addition, the reaction mixture was kept at reflux for another 8 h. The resulting solution was cooled down and filtered. The filtrate was then concentrated to around 50 mL under vacuum and poured into 400 mL of vigorously stirring water containing 5 mL of conc. hydrochloric acid. The white precipitate was collected by filtration and washed consecutively with 400 mL of water and 100 mL of CH_3OH. The cyclic oligomers were dried in a vacuum oven at 150 ℃ for 24 h (4.9 g ,96% yield). ^{1}H-NMR δ 8.6 (b, 1H), 7.93 (m, 2H), 7.85-7.81 (m, 5H), 7.75-7.66 (m, 6H), 7.56 (b, 1H), 7.48 (b, 2H), 7.21-7.18 (m, 2H), 7.15-7.10 (m, 2H).

Cyclic oligomers 9.10a.

^{1}H-NMR δ 7.70 (m, 2H), 7.64 (m, 4H), 7.56 (m, 5H), 7.48 (b, 2H), 7.12 (d, 4H), 7.06 (d, 4H).

Cyclic oligomers 9.10b.

^{1}H-NMR δ 7.68-7.64 (m, 2H), 7.60-7.50 (m, 5H), 7.45 (m, 2H), 7.26-7.21 (m, 4H), 7.02-7.00 (m, 4H), 6.97-6.94 (m, 4H), 1.65 (m, 6H).

Cyclic oligomers 9.10c.

^{1}H-NMR δ 7.69-7.65 (m, 2H), 7.63-7.53 (m, 5H), 7.47 (m, 2H), 7.35-7.34 (m, 4H), 7.08-7.03 (m, 4H), 7.00-6.98 (m, 4H).

Cyclic oligomers 9.10d.

^{1}H-NMR δ 7.80-7.75 (m, 2H), 7.66-7.60 (m, 2H), 7.60-7.51 (m, 5H), 7.50-7.35 (m, 6H), 7.30-7.27 (m, 2H), 7.23-7.18 (m, 4H), 7.02-6.98 (m, 4H), 6.94-6.87 (m, 4H).

Synthesis of linear oligomers 9.13.

A 50 mL three neck flask equipped with a Dean-Stark trap and condenser, and a nitrogen inlet was charged with bis(4-fluorophenyl)phenylphosphine oxide (1.2571 g, 4.0 mmol), **3** (0.9530g, 4.0 mmol), anhydrous K_2CO_3 (1.10g, 8.0 mmol), DMAc (10 mL), and toluene (6 mL). The mixture was kept at reflux for 1 h to remove the water formed and then the toluene was removed. The resulting mixture was kept at reflux further for 1 h, cooled down, and filtered into 200 mL of water containing 5 mL of concentrated hydrochloric acid. The white precipitate was filtered and washed with 200 mL of water and then 100 mL of CH_3OH. The desired linear oligomers **9.13** were obtained in 1.99 g (yield, 97%) after drying in vacuo at 100 °C for 24 h.

Melt ring-opening polymerization of cyclic oligomers 9.10a.

Cyclic oligomers **9.10a** (0.5 g) was dissolved in a minimum amount of $CHCl_3$, and to this solution a potassium 4,4'-biphenoxide solution (0.30 mL) in CH_3OH (10 mg/mL) was added. The solution was evaporated and dried at 100 °C for 24 h. The dried powder was put in a 10 mL test tube equipped with a nitrogen inlet. The test tube was then placed in a salt bath preheated to 350 °C for 45 min and cooled down. The resulting material is readily soluble in $CHCl_3$. However, in contrast to its cyclic oligomers , it is not soluble in THF.

9.7. References and notes

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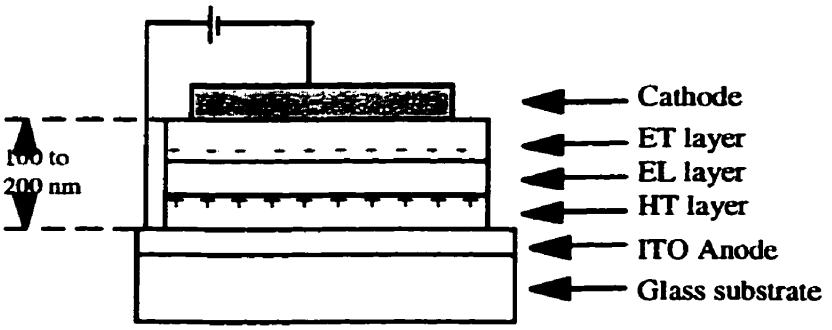
Chapter 10. Synthesis of Highly Fluorescent Materials: Isoindole Containing Polymers

10.1. Introduction

Organic light emitters have gained momentum during recent years and have become closer to commercialization.[1,2] Interest in organic light-emitting diodes (LEDs) was kindled by Tang and Van Slyke with their multilayer device (Figure 10.1).[3]

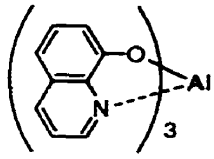


ET: Electron transport
EL: Electroluminescent
HT: Hole transport
ITO: Indium-Tin-Oxide

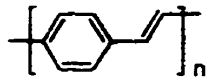
Figure 10.1. A typical three-layer LED device

A variety of low-molar-mass organic materials have been used as the emitter layer to build the LED devices.[4] The most commonly reported example is tris(8-hydroxy-quinolinate)aluminum (Alq_3)(**10.1**). However, the crystallization of small molecules results in low stability and relatively high voltage requirement.[5,6] The use of a polymeric material as the light emitter was reported by Burroughes.[5] They reported that poly(*p*-phenylenevinylene) (PPV) (**10.2**) sandwiched in an ITO/PPV/metal device emits visible light. This led to the preparation of various PPV derivatives with the objective of increasing quantum yields and modifying the visible spectrum.[6-9] Two different approaches have been adopted for the synthesis of electroluminescent (EL) polymers. One is the use of fully conjugated or segmentally conjugated main chain

polymers as the EL source, while another one is the use of polymers with side chain chromophores attached. Other conjugated systems have been studied as the light emitting layer, *e. g.* poly(*p*-phenylene) (PPP) (**10.3**) and its derivatives,[10-11] poly(*p*-phenylene ethynylene)s (**10.4**),[12,13] poly(oxadiazole)s (**10.5**),[14,15] poly(2,5-thienylene)s (**10.6**).[16,17] These polymeric materials all have low electroluminescent quantum yields.[5]



10.1



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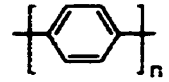
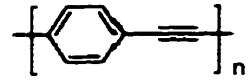


10.3



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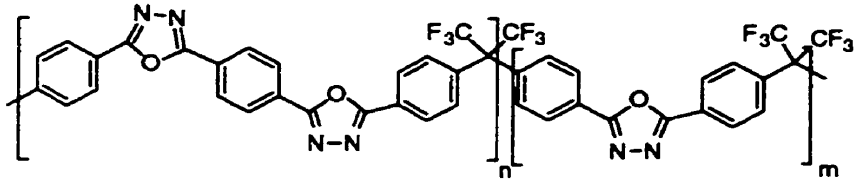
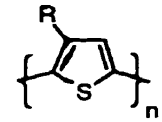


10.5



10.6

Photoluminescence (PL) and electroluminescence spectra are nearly always identical,[2] and a comparison study of EL and PL efficiencies of a LED device has been carried out.[18] Generally, a higher efficiency for an EL material is obtainable with a PL material with higher efficiency. One can use this as a guide for the design of new polymeric EL materials for LED devices by screening for organic chromophores with high PL quantum yields.

10.2. Strategy and goals

Several years ago, a series of high performance polymers containing the *o*-dibenzoylbenzene moiety were synthesized in this laboratory.[19] We became interested in transforming these polymers into the corresponding isoindole containing polymers, which could be potentially very good fluorescent and electroluminescent materials. It is well documented that isoindoles are strongly fluorescent compounds with high

quantum yields.[20] The elegant synthesis of isoindoles by the reaction of phthalaldehyde and an amine in the presence of an alkylthiol has been used as the basis of a sensitive detection method for amines, such as amino acids, peptides and proteins.[21-24] Poly(N-methylisoindole), which shows interesting optical, electrochromic and conducting behavior, has been synthesized by chemical and electrochemical methods.[25] In this chapter, we describe the synthesis and characterization of some novel highly fluorescent isoindoles and isoindole containing polymers.

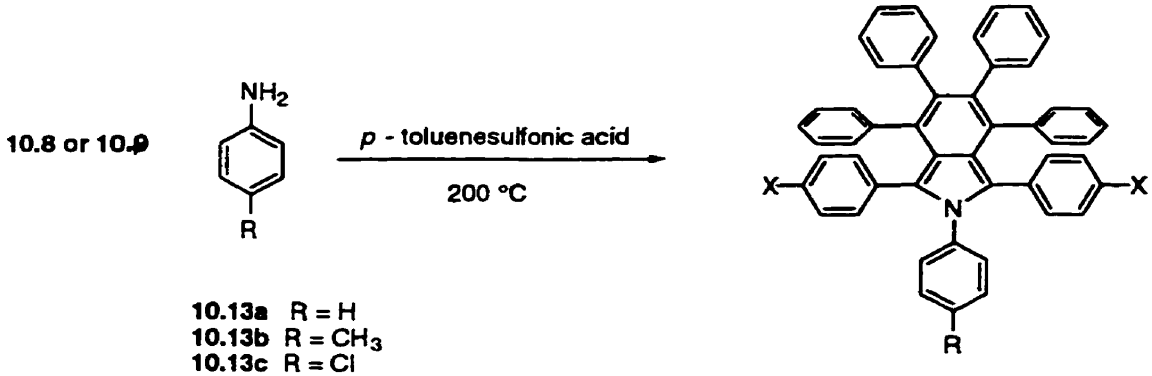
10.3. Synthesis of highly phenylated isoindoles.

1,3-Diphenylisoindole can be prepared from *o*-dibenzoylbenzene by treatment with ammonium formate[20] or with methyl amine and sodium borohydride.[26] The latter method is more appealing because of the mild conditions and high yields. We initially decided to adopt this method to transform the three 1,2-dibenzoylbenzene monomers (**10.7a-c**) into isoindole monomers. By treating with methylamine and sodium borohydride, compound **10.7a** affords an 83% yield of the isoindole (Scheme 10.1). However, when we attempted to synthesize isoindoles from 1,2-dibenzoyl-3,4,5,6-tetraphenylbenzene (**10.8**), as well as **10.7b-c**, both of the aforementioned methods failed to give satisfactory yields under various reaction conditions. The highly substituted isoindoles were of more interest because they are more stable than the non-substituted ones.[27] In a survey of the literature, there is no report on the preparation of the 1,2,3,4,7-pentaphenyl isoindoles. We have now found that high yields of highly phenylated isoindoles can be obtained by treating **10.8** with anilines under nitrogen atmosphere in the presence of catalytic amounts of *p*-toluenesulfonic acid at 200 °C for 2-4 h (Scheme 10.2). This reaction was first disclosed by Olliéro and Solladié for the formation of a 1,3-diphenyl isoindole.[28] The reaction was carried out by using excess of the aniline as the solvent. Generally, the weight ratio of aniline to **10.8** used was 3 : 1. After the reaction, the unreacted aniline as well as the side products can be easily removed by washing with methanol. Colorless highly phenylated isoindoles were obtained after further recrystallization. When 2-chloroaniline was used, the starting material **10.8** was recovered with no indication of formation of any fluorescent product. This indicates that the ortho chlorine atom hindered the formation of the isoindole, since the molecular model indicates that the resulting isoindole would be highly strained. More than 90% of **10.9** has been transformed into **10.15** after 3 hours by reaction with *p*-toluidine .

10.7a	X = F, R_1 = H, R_2 = H
10.7b	X = F, R_1 = Ph, R_2 = H
10.7c	X = F, R_1 = Ph, R_2 = Ph
10.8	X = H, R_1 = Ph, R_2 = Ph
10.9	X = OPh, R_1 = Ph, R_2 = Ph

10.10a	X = F, R_1 = H, R_2 = H
10.10b	X = F, R_1 = Ph, R_2 = H
10.10c	X = F, R_1 = Ph, R_2 = Ph
10.11	X = H, R_1 = Ph, R_2 = Ph
10.12	X = OPh, R_1 = Ph, R_2 = Ph

Scheme 10.1. Attempted synthesis of isoindoles form methylamine.



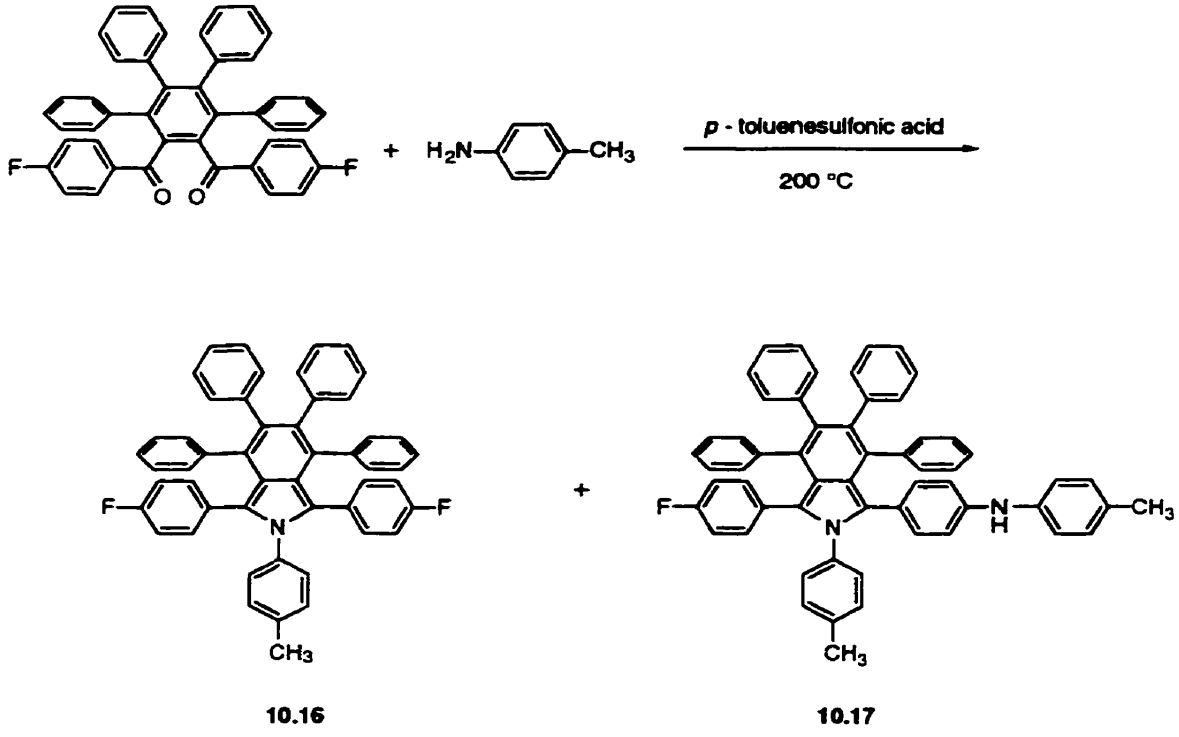
10.13a	R = H
10.13b	R = CH_3
10.13c	R = Cl

10.14a	X = H, R = H
10.14b	X = H, R = CH_3
10.14c	X = H, R = Cl
10.15	X = OPh, R = CH_3

Scheme 10.2. Synthesis of N-arylisoindoles catalyzed by *p*-toluenesulfonic acid.

When 1,2-bis(4-fluorobenzoyl)-3,6-diphenyl benzene (**10.7b**) or 1,2-bis(4-fluorobenzoyl)-3,4,5,6-tetraphenyl benzene (**10.7c**) was used as the reactant, poor yields of the expected isoindoles were obtained due to a nucleophilic substitution reaction between the aniline and the activated fluorine atoms. The reaction products are complex and difficult to purify. The formation of **10.17** was confirmed by Matrix-Assisted-Laser-Desorption/Ionization Time-of-Flight Mass Spectrometry (MALDI-TOF-MS). In the MALDI MS spectrum, there are two peaks at 699 and 785 Da,

corresponding to the molecular masses of **10.16** and **10.17**, respectively. The calculated molecular masses for **10.16** and **10.17** are 699.27 and 786.34.



10.16 **10.17**

Scheme 10.3. Reaction between a diketone containing activated fluorine atoms and *p*-toluidine.

The highly phenylated isoindoles are very stable in air in the solid sate. There is no indication of oxidation even after prolonged heating at 100 °C in air. This can be inferred from their molecular structures. The optimized structure of **10.14b** is shown in Figure 10.2. One can see that the isoindole moiety is surrounded by phenyl rings which would make it difficult to react with other reagents.

Isoindoles **10.14a-c** and **10.15** are highly fluorescent compounds, giving a blue emission under UV light. The UV-vis spectra of **10.14b** and **10.15** are shown in Figure 10.3 and the maximum emission wave numbers (λ_{em}) of these isoindoles are listed in Table 10.1. There were only minute observed changes in the emission spectra with isoindoles synthesized with different anilines.

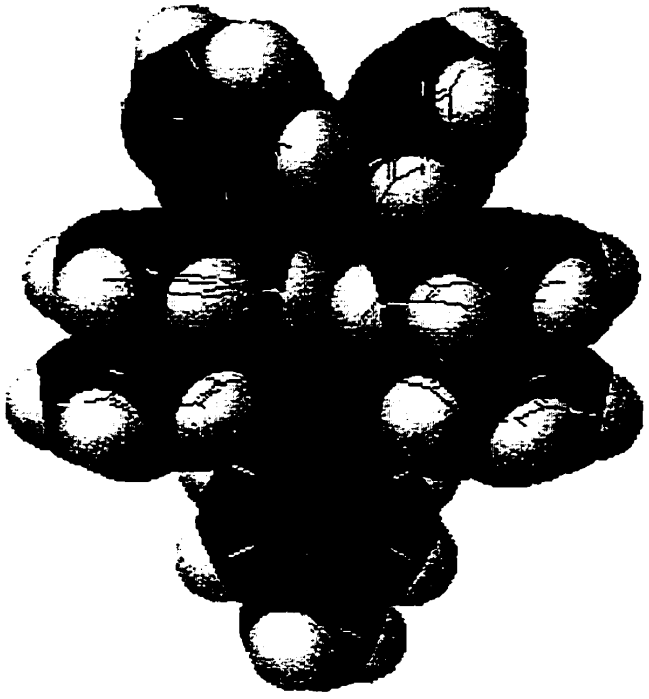


Figure 10.2. Optimized structure of isoindole **10.14b**.

Table 10.1. Maximum emission wavenumbers of highly phenylated isoindoles.

Compound	Maximum Emission Wavenumber (nm)
10.14a	456
10.14b	456
10.14c	454
10.15	470

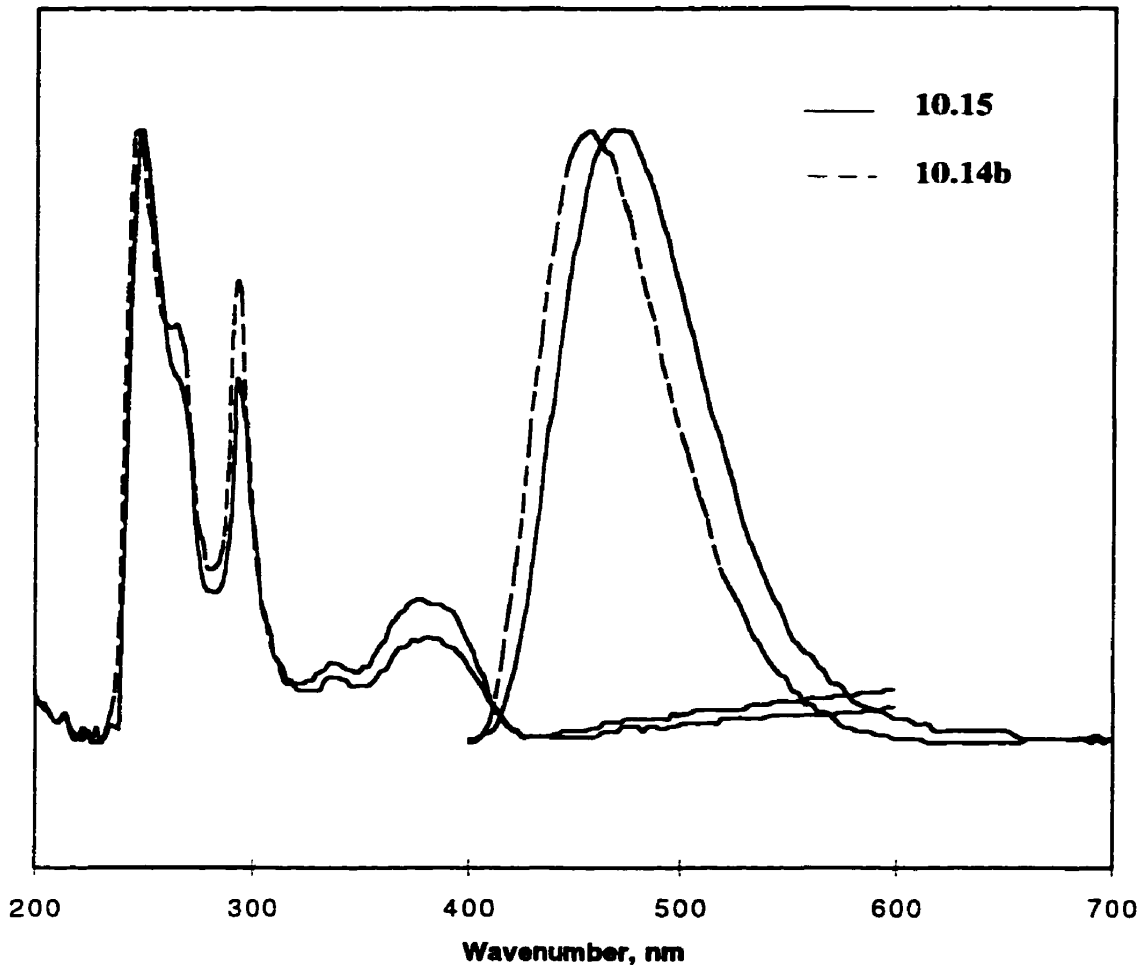
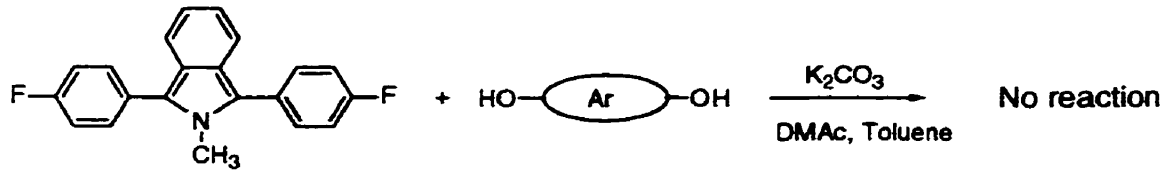


Figure 10.3. Excitation and emission spectra of isoindoles **10.14b** and **10.15** in THF solution.

10.4. Isoindole containing polymers.

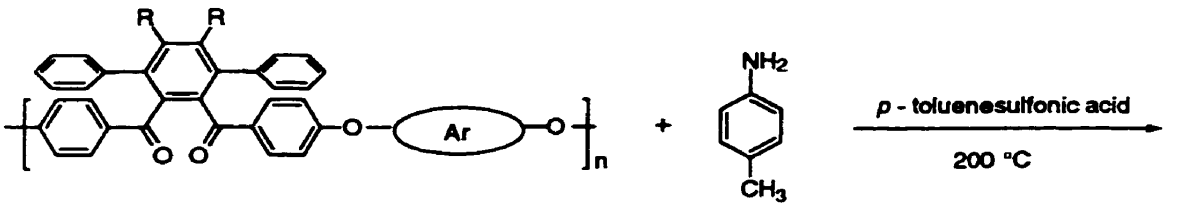
Attempted polymerization of **10.10a** with variety of bisphenols failed to give any polymer (Scheme 10.4). This was not unexpected because the isoindole moiety is electron rich and functions as an electron-donating group instead of an electron-withdrawing group. The fluorine atoms in the compound are therefore not activated.



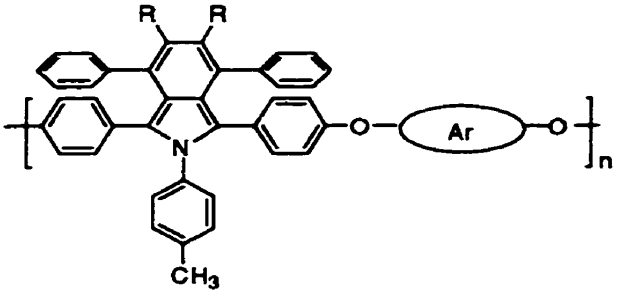
Scheme 10.4. Attempted polymerization between an isoindole monomer and bisphenols.

Our attention was then focused on the synthesis of polyisoindoles from polymer precursors. The uses of a polymer precursor to prepare heterocyclic containing polymers has been extensively used in this laboratory as well as others. For example, poly(phthalazine)s,[29] poly(isoquinoline)s,[30] and poly(2,5-pyrrole)[31] have been synthesized from their respective diketone precursor polymers. We selected *p*-toluidine as the reactant for the synthesis of a series of isoindole containing polymers.

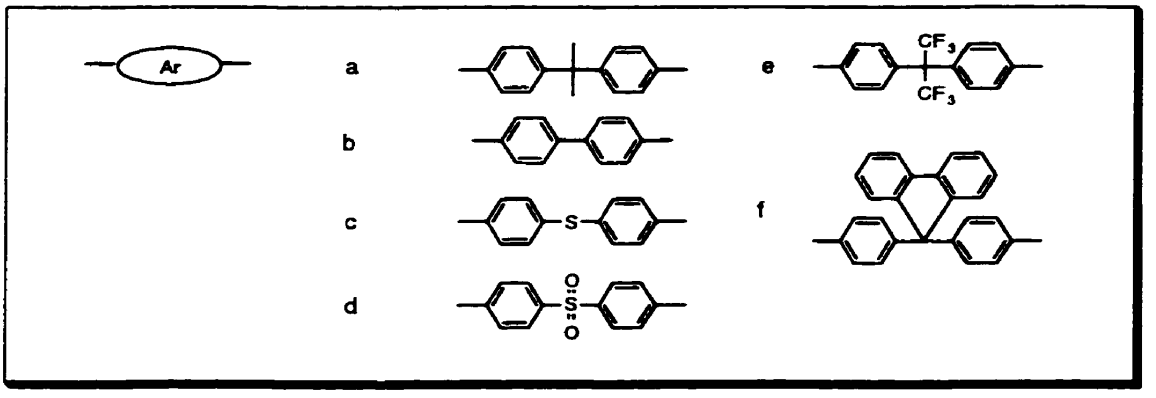
The reactions were carried out in bulk *p*-toluidine solution using 0.5 g of starting polymer. A catalytic amount of *p*-toluenesulfonic acid was used as the catalyst to effect the reaction. After 5 hours of reaction, light yellow high molecular weight poly(isoindole)s were obtained. The conversion of the diketone to the isoindole moiety was confirmed by ^{1}H-NMR. A new peak corresponding to the methyl group in the isoindole moiety appeared around δ 2.1 ppm while the peaks corresponding to the phenyl group adjacent to the ketone groups disappeared or diminished. A comparison of the ^{1}H-NMR spectrum of a poly(isoindole) with the starting material is shown in Figure 10.4. The relative ratios of the methyl group protons and the aromatic protons was used to calculate the conversion of the isoindoles from the starting polymers (Table 10.2). From Table 10.2, one can see that a quantitative conversion was obtained for almost every polymer listed. Attempts at preparation of poly(isoindole)s from non-phenyl substituted poly(ketone)s were unsuccessful. Very low molecular weight fluorescent materials were obtained in every case.



10.18a-f R = H
10.19a-f R = Ph



10.20a-f R = H
10.21a-f R = Ph



Scheme 10.5. Synthesis of isoindole containing polymers from polymeric precursors.

Table 10.2. Properties of isoindole containing polymers.

Polymer	T_r (°C)[a]	TGA (°C)[b]	Conversion[c] (%)	λ_{em} (nm)[d]	η_{inh} (dL/g)[e]	η_{inh} (dL/g)[f]
10.20a	244	498	100	488	0.55	0.61
10.20b	261	495	100	486	0.43	0.50
10.20c	248	466	100	480	0.38	0.37
10.20e	223	511	95	480	0.41	0.50
10.20f	272	502	100	488	0.45	0.55
10.21a	255	487	80	468	0.74	0.67
10.21b	275	473	90	468	0.81	0.84
10.21c	254	457	90	466	0.51	0.59
10.21d	277	472	100	462	0.43	0.37
10.21e	253	511	90	466	0.55	0.60
10.21f	294	475	85	468	0.73	0.85

a. Obtained by DSC under nitrogen atmosphere with heating rate of 20 °C/min.

b. 5 % weight loss temperature. Obtained by TGA under nitrogen atmosphere with heating rate of 20 °C/min.

c. Conversion of isoindoles in a polymer chain, estimated from ^{1}H-NMR.

d. Maximum emission wavenumber.

e. Viscosities of poly(isoindole)s measured at a concentration of 0.5 g/dL in $CHCl_3$ at 25.0 °C.

f. Viscosities of precursor polymers measured at a concentration of 0.5 g/dL in $CHCl_3$ at 25.0 °C.

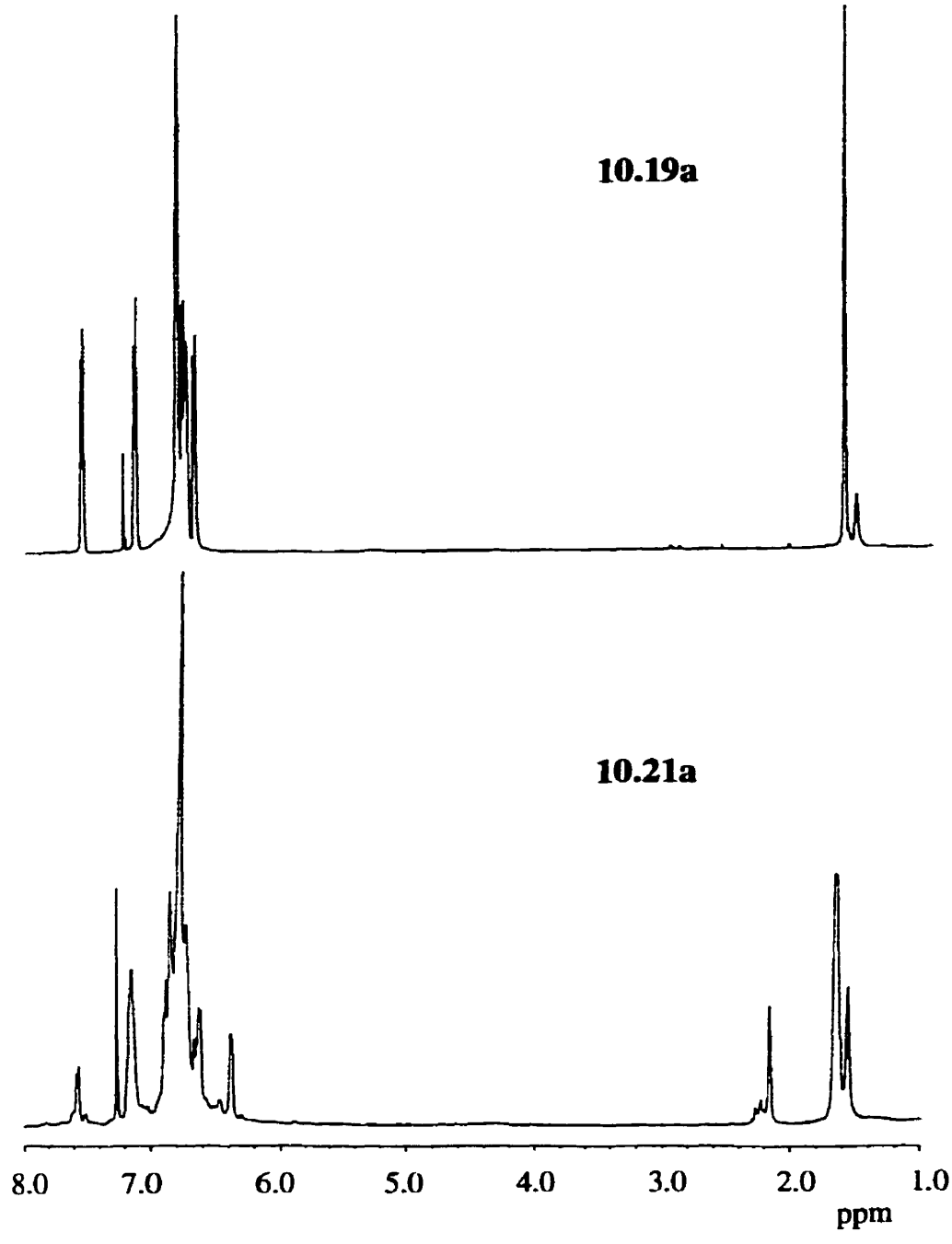


Figure 10.4. ^{1}H-NMR spectra of isoindole containing polymer **10.21a** and its precursor **10.19a.**

Attempts to obtain useful molecular weight information from GPC were unsuccessful. A comparision of the GPC profiles between a starting polymer and the resulting polymer is shown in Figure 10.5. Due to the formation of the bulky isoindole groups and the decreased flexibility of the polymer chain, the apparent molecular weights as measured by GPC of the poly(isoindole)s were extremely large. The same phenomena has been observed in a previous study for the transformation of a poly(ketone) into a poly(phthalazine) or a poly(isoquinoline). Enormous apparent molecular weights were observed from GPC.[32] Solution viscosities were then measured, which are listed in Table 10.2. The inherent viscosities of the poly(isoindole)s are in the range of 0.38 - 0.81 dL/g measured in $CHCl_3$ at 25 °C at a concentration of 0.5 g/dL. This indicates that the poly(isoindole)s are high molecular weight. There is no significant change in inherent viscosities between starting polymers and the resulting poly(isoindole)s, which indicates that no serious decomposition took place due to the nucleophilic property of the aniline which could potentially break down the polymer chains.[33]

The poly(isoindole)s **10.20a-f** and **10.21a-f** have very high glass transition temperatures (T_gs) between 223-294 °C (Table 10.2) It was unexpected that the values are more than 10 °C lower than the corresponding precursors. Both poly(isoquinoline)s and poly(phthalazine)s, which were also obtained from the conversion of the diketone polymers, have higher T_gs than their diketone precursors. However, the poly(isoquinoline)s have lower T_gs than the corresponding poly(phthalazine)s, which may be due to the pendent phenyl group in these poly(isoquinoline)s.[29,30] In the present case, the extra pendent methyl group in poly(isoindole)s may be responsible for the lowering of the T_gs of the poly(isoindole)s. Thermal stabilities of poly(isoindole)s also decreased as compared with the precursors as indicated from TGA measurements. However, the 5% weight loss temperatures of poly(isoindole)s synthesized here are still in the range of 457 - 511 °C, indicating that they are thermostable polymers.

As expected, the poly(isoindole)s obtained are highly fluorescent materials. The UV-vis and emission spectra of **10.20b** and **10.21b** are shown in Figure 10.6. The maximum emission wave numbers of other poly(isoindole)s are listed in Table 10.2. The maximum emission wave numbers for the tetraphenyl substituted isoindole containing polymers are around 468 nm, while those of diphenyl subsituted isoindole containing polymers are around 486 nm. Two conclusions can be draw from Table 10.2. First, the color of the emission light does not change with the changing of the

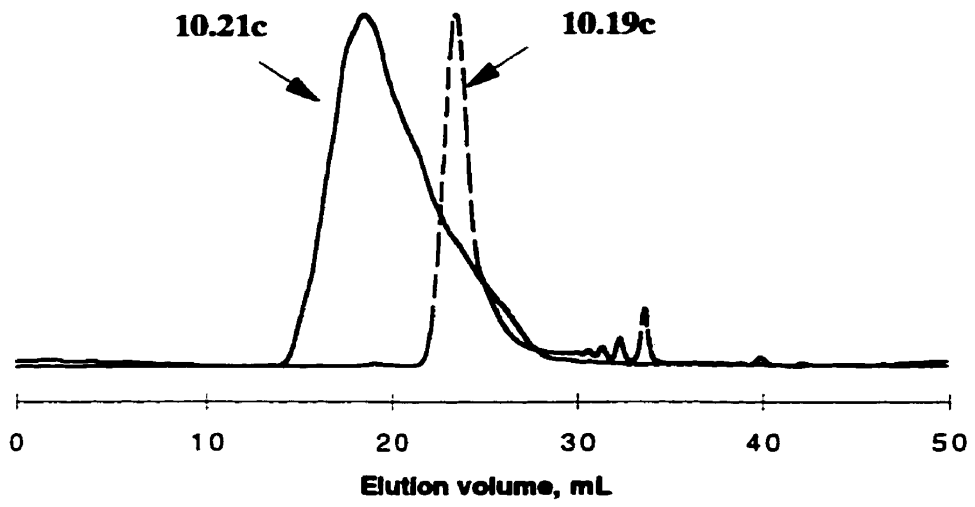


Figure 10.5. A comparision of GPC between an isoindole containing polymer and its precursor

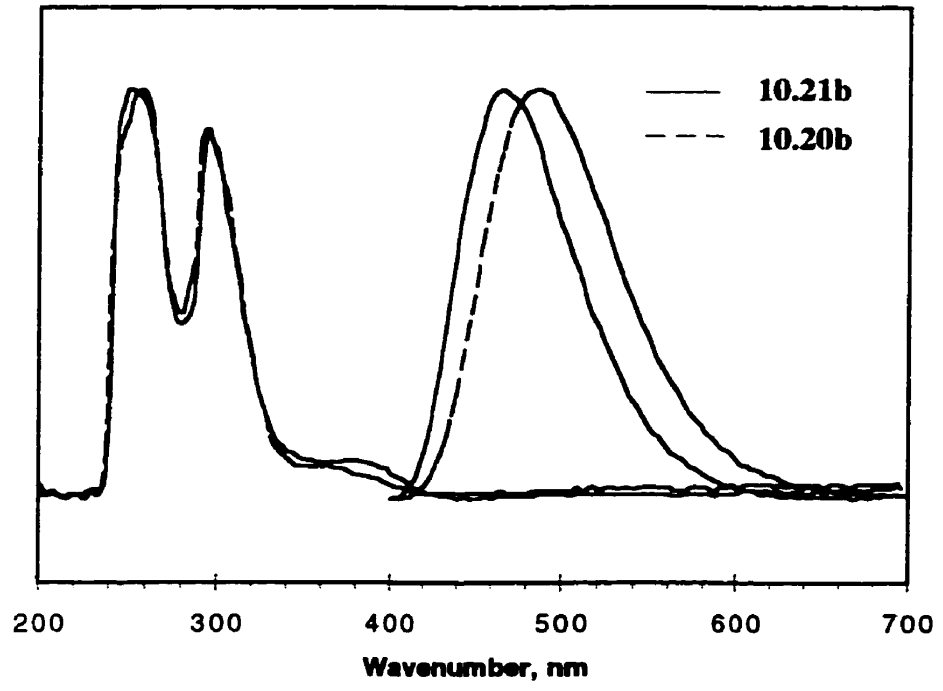


Figure 10.6. Excitation and emission spectra of isoindole containing polymers **10.20b** and **10.21b** in THF solution.

bisphenol monomer. Second, tetraphenyl substituted poly(isoindole)s have emission frequencies at shorter wave numbers than diphenyl substituted poly(isoindole)s.

10.5. Conclusions

Highly phenylated isoindoles can be prepared by reaction between a highly phenylated diketone and anilines at 200 ℃ in the presence of a catalytic amount of *p*-toluenesulfonic acid. These isoindoles are highly fluorescent and their emission frequencies do not change significantly with the different substituents on the aniline moiety. However, the emission frequencies change with different numbers of substitutents on the isoindole moiety.

High molecular weight diphenyl and tetraphenyl substituted poly(isoindole)s have been obtained by treating the respective diketone polymers with *p*-toluidine at 200 ℃ in the presence of a catalytic amount of *p*-toluenesulfonic acid under nitrogen atmosphere. From the ^{1}H-NMR spectra, the conversions to isoindoles are almost quantitative. The high inherent viscosities of the polymers indicated that the poly(isoindole)s are high molecular weight polymers. These poly(isoindole)s are highly fluorescent materials and their fluorescent spectra have been measured. This series of materials are potentially candidates for electroluminescent materials for the fabrication of organic LEDs.

10.6. Experimental section

Materials

All anilines were purchased from Aldrich Chemical, Inc. and distilled under nitrogen prior to use. The starting materials **10.7a-c**,[19] **10.8**[34] and **10.9**[35] were prepared according to previously published procedures. Polymers **10.18a-f** and **10.19a-f** were prepared according to previously reported methods.[19]

Measurements

Melting points were measured on a Mettler FP 80 DSC with heating rate of 5 ℃/min. T_gs were determined on a Seiko 220 DSC instrument at a heating rate of 20℃/min under a nitrogen atmosphere (flow rate 160 mL/min). Thermogravimetric analysis (TGA) data were obtained using a Seiko TG/DTA instrument at a heating rate

of 20°C/min in nitrogen (flow rate 200 mL/min). The ^{1}H-NMR spectra were recorded on a Varian Unity 500 NMR instrument in $CDCl_3$. The chemical shifts of protons were calibrated with tetramethylsilane (TMS) and are quoted in *ppm*. Size exclusion chromatography (SEC) was performed on a Waters 510 HPLC equipped with 5μ phenogel columns (linear, 3 x 500 Ä) arranged in series and a UV detector at 254 nm. Chloroform was used as eluent and polystyrene standards were used to calibrate the machine. Inherent viscosities were measured using chloroform solution at a concentration of 0.5 g/dL in a Ubbelohde viscometer. MALDI-TOF MS were recorded on a Kratos Kompact MALDI-III TOF instrument with a maximum laser output of 6 mW at a wavelength of 337 nm. Elemental analyses were performed by Fine Analysis Laboratories Ltd., Halmiton, Ontario.

Absorption and fluorescence measurements were performed in THF solution in a standard quartz cell, using a Hewlett Packard 8452 diode array spectrophotometer equipped with a Lauda RM6 thermostat and a Spex Fluorolog spectrofluorometer, respectively. Emission spectra were corrected for both the fluctuation of the incident light intensity and the response of the detector as a function of wavelength, using a solution of rhodamine-B as internal reference and correction factors provided by the manufacturer, respectively. Slit widths of 0.3 and 2.0 mm for the excitation and detection monochromators were chosen, respectively. The wavenumber of the excitation light was set at 375 nm.

The optimized structure of **10.14b** was obtained from a CAChe molecular mechanics program running on a Macintosh desktop computer.

Synthesis of 10.10a. A pellet of $NaBH_4$ (0.24 g, 6.3 mmol) was added to 15 mL of an ethanol solution containing 1.0 g (3.1 mmol) of 1,2-bis(4-fluorobenzoyl)benzene and 15 mL of 40% aq. methylamine solution. The resulting mixture was kept at reflux for 1.5 h and cooled down to room temperature. The yellow precipitate was filtered and recrystallized from ethanol. Yield, 0.82g (83%). m.p. 72-74 °C. ^{1}H-NMR ($CDCl_3$) δ (ppm) 7.54-7.50(m, 6H), 7.24-7.20 (m, 4H), 7.00-6.98 (q, 2H0, 3.83 (s, 3H). MALDI-TOF-MS, *m/z* found, 319, calcd. for $C_{21}H_{15}F_2N$, 319.

General procedure for the synthesis of highly phenylated isoindoles. A typical example is given as follows. A 50 mL three neck flask equipped with a nitrogen inlet, a thermometer, a condenser and a magnetic stirrer was

charged with **10.8** (1.0 g, 1.69 mmol), *p*-toluidine (3.0 g, 28 mmol), and *p*-toluenesulfonic acid monohydrate (0.1 g, 0.5 mmol). The mixture was kept at 200 °C for 2 h and then the resulting dark red solution was cooled down to room temperature, to which 50 mL of methanol was added. The solid precipitate was filtered and washed with 20 mL of methanol three more times. The white solid was then recrystallized from toluene to yield 0.83 g (77 %) of pure isoindole product (**10.14b**). m.p. 370 °C. ^{1}H-NMR ($CDCl_3$) δ (ppm) 6.84-6.62 (m, 34H), 2.14 (s, 3H). MALDI-TOF-MS, *m/z* found, 662, calcd. for $C_{51}H_{37}N$, 663. Anal. Calcd for $C_{51}H_{37}N$: C, 92.27; H, 5.62; N, 2.11. Found: C, 92.42; H, 5.60; N, 2.22.

10.14a. yield, 53%. m.p. 289 °C. ^{1}H-NMR ($CDCl_3$) δ (ppm) 7.00-6.62 (m, 35H). MALDI-TOF-MS, *m/z* found, 648, calcd. for $C_{50}H_{35}N$, 649. Anal. Calcd for $C_{50}H_{35}N$: C, 92.42; H, 5.43; N, 2.16. Found: C, 92.00; H, 5.45; N, 2.49.

10.14c. yield, 62%. m.p. 343 °C. ^{1}H-NMR ($CDCl_3$) δ (ppm) 6.97-6.64 (m, 34H). MALDI-TOF-MS, *m/z* found, 683, calcd. for $C_{50}H_{34}ClN$, 683. Anal. Calcd for $C_{50}H_{34}ClN$: C, 87.76; H, 5.01; N, 2.05. Found: C, 87.68; H, 5.06; N, 2.48.

10.15. yield, 70%. m.p. 288 °C. ^{1}H-NMR ($CDCl_3$) δ (ppm) 7.31 (t, 4H, J = 8.3 Hz), 7.07 (t, 2H, J = 7.3 Hz), 6.93-6.75 (m, 26H), 6.68-6.64 (m, 6H), 6.39 (d, 4H, J = 8.3 Hz), 2.19 (s, 3H). MALDI-TOF-MS, *m/z* found, 846, calcd. for $C_{63}H_{45}NO_2$, 847. Anal. Calcd for $C_{63}H_{45}NO_2$: C, 89.23; H, 5.35; N, 1.65. Found: C, 88.76; H, 5.36; N, 2.02.

General procedure for the synthesis of highly phenylated isoindole containing polymers. A typical example is given as follows. Polymer **10.18c** (0.50 g) and *p*-toluidine (3.0 g) were mixed and kept at 200 °C for 5 h under notrogen atmosphere in the presence of a catalytic amount of *p*-toluenesulfonic acid (0.03 g). The dark colored mixture was then cooled down to room temperature, diluted with 10 mL of $CHCl_3$ and poured into 100 mL of methanol to precipitate out the polymer. The polymer was collected by filtration, redissolved in 10 mL of chloroform and precipitated out from 100 mL of methanol. This process was repeated three times

and the chloroform solution was filtered through a thin layer of celite the last time. The polymer collected was dried at 100 °C in vacuo for 24 h to give 0.35 g (yield, 64%) of light yellow poly(isoindole) **10.21c**. The low yield is due to mechanical loss.

10.7. References and notes

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