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Synthesis and Characterization of Novel Polycyclic Structures, Precursors to High Performance Polymers

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

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0-612-44509-7

Canadä

To: my parents, sister and brother

Acknowledgements

I am, forever, indebted to my supervisor Prof. Allan S. Hay for his constant and unfailing help, guidance and patience throughout the course of my PhD program. His intuition and enthusiasm in chemistry have contributed a great deal toward my knowledge and understanding of new chemical syntheses.

Thank you Gerry for helping me with the operation and maintenance of different polymer characterization instruments. My thanks to Yi-feng for providing the commercial siloxane gum samples and for many interesting tennis games.

I would also like to thank my colleagues in Lab 409 both past and present: Martino, Pong, Coromoto, Ed, Hossein, Gao, Haixin, Charlie, Asfia, Antisar, Imad, Shu, Ding, Jin, Linghua, Yue Sun, Jianping and Meng for an amicable work environment, support, and friendships.

My thanks and appreciations also go to Shanti and Ilie for helping me with the low temperature differential scanning calorimetry instrument.

I would like to extend my thanks to Bushra and Arlène for the french translation of the abstract. Thanks to Dr. Francoise Sauriol for her help with different NMR instruments. Also to Fred (machine shop) and Rick (electronics shop), thank you for your help with the upkeep of equipment.

Finally, financial support by the Natural Sciences and Engineering Research Council of Canada is gratefully acknowledged.

Abstract

Our primary goal in this thesis was to develop convenient methods for the synthesis of oligomeric polycyclics which could be ring-opened at elevated temperatures in the presence of a catalyst to give new classes of thermoset materials.

A simple and commercially attractive approach was utilized to synthesize novolac type resins by reacting p-substituted phenols with formaldehyde using a cation exchange resin as catalyst in the presence of chlorobenzene as solvent.

Novel oligomeric polycyclic carbonates were prepared by reacting the multifunctional phenol-formaldehyde resin with excess triphosgene under high dilution conditions. When the oligomeric polycyclic carbonates were heated at elevated temperatures using an initiator, a highly cross-linked network was obtained. In addition, the polycyclics were mixed with a commercial BPA polycarbonate and cured at different temperatures in the presence of a catalyst. When the mixture of BPA polycarbonate with 10 wt. % polycyclic carbonate was cured at 350 °C for 30 min. using a catalytic amount of lithium stearate, it gave a highly cross-linked network.

Two series of polycyclic phosphonates were synthesized by reacting the oligomeric phenol-formaldehyde resins with phosphonic dichlorides under high dilution conditions in a polar aprotic solvent. The polycyclic phosphonates were similarly subjected to ringopening polymerization at elevated temperatures in the presence of an initiator. The crosslinked phosphonates exhibited good flame retardance properties.

Two classes of oligomeric siloxane resins were also synthesized by reacting the phenol-formaldehyde novolac type resins with dialkyl or diaryl dichloro silanes under high dilution conditions. The formation of predominantly polycyclic siloxane structures was revealed by MALDI-TOF MS, Gradient HPLC and ¹H NMR. Blends of commercial polysiloxane gums with different proportions of polycyclic siloxane resins were subjected

to curing at 300 °C in the presence of KOH catalyst. Polysiloxane gums are highly unstable at 300 °C in the presence of a basic catalyst. However, the cross-linked polysiloxane gum at 30 wt% loading of polycyclic siloxanes, was sufficiently stable at this temperature.

A Bisphenol A dimer (o, o' methylene bridged) was synthesized by a single-pot reaction between formaldehyde and excess BPA using cation exchange resin catalyst. A few novel classes of oligomeric polycyclics with low melt viscosities were synthesized from this dimer under high dilution conditions.

A series of co-polycarbonates of BPA were synthesized by the reaction of methylene bridged dimer with BPA and triphosgene. An alternative *in-situ* polymerization method was also developed to synthesize the BPA co-polycarbonates. These co-polymers containing cross-linkable cyclic carbonate moieties on the backbone, gave thermoset materials when cured at elevated temperatures in the presence of a catalyst.

Low molecular weight poly(aryl ether sulfone)s end-capped with metallophthalocyanine moieties were prepared by reacting poly(aryl ether sulfone)s containing o-phthalonitrile end-groups with excess phthalonitrile and metals/metal salts in quinoline. These polymers were characterized in detail by using IR, UV-VIS, ¹H NMR and GPC techniques. Annealing studies on the polymers containing PcM end-groups were undertaken in order to investigate the occurrence of stacking of phthalocyanine rings in the melt. This study was conducted by using a Thermo-Gravimetric/Differential Thermal Analysis (TG/DTA) instrument.

Sommaire

Le premier but dans cette thèse a été de développer des méthodes convenables pour la synthèse d'oligomères polycycliques qui peuvent subir une ouverture de cycle à hautes températures ou en présence de catalyseurs pour donner de nouvelles classes de matériaux.

Une simple approche, commercialement attirante, a été de synthétiser des résines de type "novolac" par réaction de p-phénol substitué et le formaldehyde, en utilisant une résine à échange cationique comme catalyseur en présence de chlorobenzène comme solvant.

Des oligomères carbonates originaux ont été preparés par réaction de résines phénol-formaldehyde multifonctionnalisées avec un excès de triphosgène dans des conditions de haute dilution. Quand les oligomères polycycliques carbonates sont chauffés à hautes températures utilisant un initiateur, un réseau comportant des liaisons transversales est obtenu. De plus, les polycycliques ont été mélangés avec un BPA polycarbonate commercial et soumis à différentes températures en présence d'un catalyseur. Quand le mélange de BPA polycarbonates avec 10% de carbonates polycycliques est chauffé à 350 °C pendant 30 min, utilisant une quantité catalytique de lithium stéarate, un réseau comportant des liaisons transversales est obtenu.

Deux séries de phosphonates polycycliques ont été synthétisés par réaction de résines phénol-formaldéhyde oligomères avec des dichlorures méthyl et phénylphosphoniques dans des conditions de haute dilution dans un solvant polaire aprotique. Les phosphonates polycycliques ont été, de la même manière, sujet à une polymérisation par ouverture de cycle à températures élevées en présence d'un initiateur. Les phosphonates ainsi liés entre eux font preuve de bonnes propriétés anti-inflammables.

Deux classes de résines siloxanes oligomères ont été aussi préparées par réaction de résines de type phénol-formaldéhyde novolac avec des dialkyl ou diaryl dichlorosilanes dans des conditions de haute dilution. La formation prédominante de structures polycycliques siloxanes a été révelée par MALDI-TOF MS, Gradient HPLC et RMN du proton. Des mélanges de gommes polysiloxanes avec différentes proportions de résines polycycliques siloxanes ont été chauffés à 300 °C en présence du catalyseur KOH. Les gommes polysiloxanes sont hautement instables à 300 °C en présence d'un catalyseur basique. Toutefois, les gommes polysiloxanes ramifiées comportant 30% en masse de siloxanes polycycliques, sont suffisamment stables à cette température.

Un dimère de biphénol A un (o, o' méthylène ponté) a été synthétisé par une réaction "one-pot" entre le formaldéhyde et un excès de BPA utilisant un catalyseur résine échangeur de cations. Quelques nouvelles classes d'oligomères polycycliques à faible viscosité de fusion, ont été synthétisées à partir de ce dimère dans des conditions de haute dilution.

Des séries de co-polycarbonates de BPA ont été synthétisées par réaction de dimère ponté par un méthylène avec le BPA et le triphosgène. Une méthode alternative de polymérisation *in-situ* a aussi été développée pour synthétiser des co-polycarbonates BPA. Ces co-polymères contenant sur leur squelette des portions carbonates cycliques susceptibles de créer des liaisons entre eux, ont donné des matériaux thermodurcissables quand ceux-ci sont chauffés à des températures élevées en présence d'un catalyseur.

Les poly(aryl ether sulfone)s, à faible poids moléculaire, terminées par une partie metallophthalocyanine, ont été préparées par réaction de poly(aryl ether sulfone)s contenant des groupes terminaux phthalonitrile avec un excès de phthalonitrile et des sels de métaux dans la quinoline. Ces polymères ont été caracterisés en détail en utilisant les techniques IR, UV-VIS, RMN ¹H et CPG. Les études de thermodureté sur les polymères contenant des groupes terminaux PcM ont été réalisées dans le but de rechercher les conditions dans lesquels les cycles phthalocyanines s'empilent dans la fonte. Cette étude a été conduite en utilisant un instrument de thermogravimétrie/analyse thermique differentielle (TG/ATD).

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Glossary of abbreviations and symbols

BPA	Bisphenol A (4, 4'-Isopropylidenebiphenol)
CDCl ₃	Deuterated chloroform
CuPc	Copper phthalocyanine
DP	Degree of polymerization
DSC	Differential scanning calorimetry
Da	Dalton
D ₂ O	Deuterated water
DMSO-d ₆	Deuterated dimethylsulfoxide
DMAc	N, N'-Dimethylacetamide
DMF	N, N'-Dimethylformamide
D ₃	Hexamethylcyclotrisiloxane
D ₄	Octamethylcyclotetrasiloxane
EtOAc	Ethyl acetate
ELN	Diethylamine
FePc	Iron phthalocyanine
GC	Gas chromatography
GPC	Gel permeation chromatography
HPLC	High performance liquid chromatography
IR	Infrared
КОН	Potassium hydroxide
LIST	Lithium stearate
LiBr	Lithium bromide

MALDI-TOF MS	Matrix assisted laser desorption ionization-time of flight mass
	spectrometry
M _n	Number average molecular weight
M,	Weight average molecular weight
Мр	Melting point
NMR	Nuclear magnetic resonance
P/F	Phenol/formaldehyde
ррт	Parts per million
PcM	Metallophthalocyanine
Pyr	Pyridine
ROP	Ring-opening polymerization
THF	Tetrahydrofuran
TMEDA	N, N, N', N'-tetramethylenediamine
TG/DTA	Thermo-gravimetric/Differential thermal analysis
UV-VIS	Ultraviolet-visible

Chapter 1. Introduction

1.1. Thermosetting and Thermoplastic Polymers

A plastic can be defined as a high molecular weight organic polymer which changes its shape on the application of a force and retains it on the removal of the force.¹ Plastics can be further subdivided into thermosetting and thermoplastic polymers. The structural differences between these two classes of plastics is closely related to the term "crosslinking". When the polymer molecules are linked to each other at points other than their ends, the polymers are termed as cross-linked.² The molecular chains are joined together by covalent bonds. Generally the number of chains that emanate from these points are required to be at least three to form a cross-link. This can be pictorially represented as shown below.



Figure 1.1. A cross-linked network

This phenomenon of cross-linking is very important from an industrial perspective. Depending on the degree of cross-linking, the polymers find uses ranging from rubbers (low degree of cross-linking in a material having low glass-transition temperature, T_g) to advanced composite materials (high degree of cross-linking in a high T_g material).

Thermosetting polymers can be defined as polymer networks which are formed after crosslinking and they are insoluble and infusible. Therefore once they are fabricated they cannot be processed any further. Generally precursor polymers/oligomers that are soluble and fusible are synthesized first and then they are transferred to a mold of desired shape and size. In the final step, a chemical reaction is initiated to form the cross-linked thermoset polymer. The major advantage of cross-linking is that it gives rise to excellent thermal stability, solvent resistance and increased dimensional stability of the network structures. On the contrary, plastics that soften and flow upon heating and are not cross-linked, are termed as thermoplastics. Thermoplastics can be remolded and reshaped many times.

Engineering thermoplastics can be classified as plastics that perform for long periods of time complying with engineering requirements for properties such as mechanical strength, heat, chemical and fire resistance. Examples of engineering thermoplastics are



Nylon 6



Polycarbonate



Polyphenylene oxide

Figure 1.2. Engineering thermoplastics

1.2. Importance of processability

To achieve significant physical and mechanical properties in a polymer, it should have sufficiently high molecular weight. The processing of polymers becomes increasingly difficult as they attain higher molecular weight because of their high melt viscosities. To obtain the final property profile of a very high molecular weight polymer with relative ease in processability is thus industrially attractive because of the low cost involved in the processing. High molecular weight polymers with very high T_g s which would be potentially useful as matrix resins for advanced composites cannot be melt processed once the processing temperatures would be in a region where some thermal decomposition may occur. Two useful ways of achieving easy processability with relevant examples are described in the following paragraphs.

1.3. Mixed oligomeric cyclics as precursors

One of the most important features of low molecular weight mixed cyclics is their low melt viscosities. Therefore, the equipment required to process these cyclic precursors is much simpler and cost effective compared to that necessary for high viscosity polymers. Generally these cyclic precursors which are low molecular weight and have low melt viscosity are transformed into high molecular weight polymers via ring-opening polymerization under the influence of heat and initiators without the release of any volatile byproducts. Another advantage of cyclic precursors is that a much higher molecular weight polymers can be obtained.

Extensive investigation on the synthesis of cyclic aromatic carbonates from o, o' biphenols and their subsequent ROP to high molecular weight polycarbonates was carried out by Prochaska ³⁻⁵ in the mid 1960s (Scheme 3.1) as described in chapter 3. Synthesis of a cyclic tetrameric carbonate of BPA (Scheme 1.1) was reported by Schnell and Bottenbruch.⁶ This was subjected to ROP at temperatures above 300 ^oC to yield high molecular weight polycarbonates.⁷



Scheme 1.1 Synthetic route to cyclic tetrameric BPA carbonate

Brunelle et al^{8,9} reported the synthesis of oligomeric cyclic carbonates of BPA by a twostep triethylamine catalysed hydrolysis/condensation reaction of BPA bis (chloroformate) (scheme 1.2). High molecular weight polycarbonates were obtained by heating the cyclics at 300 $^{\circ}$ C in the presence of an initiator.



Scheme 1.2 Synthesis and polymerization of oligomeric cyclic carbonates of BPA

Bishop and co-workers^{10,11} synthesized poly(ether sulfone) cyclooligomers by adding an AB monomer or AA + BB monomers continually to a suspension of K_2CO_3 in N, N-dimethylacetamide at 130-i40 °C (scheme 1.3).



Scheme 1.3 Synthetic route to cyclic poly(ether sulfone)s

Chan and Hay¹² developed an efficient method of synthesis of cyclic(aryl ether ketone)s containing a 1, 2- dibenzoylbenzene moiety by an aromatic nucleophilic substitution route using the AA + BB approach (scheme 1.4).



Scheme 1.4 Synthetic route to cyclic oligomeric(aryl ether ketone)s

A new class of macrocyclic aryl ether ether sulfide oligomers was synthesized in quantitative yield by Wang & Hay^{13,14} by a two step reaction.



Scheme 1.5 Synthetic route to cyclic oligomeric (aryl ether ether sulfide)s

Ding and Hay¹⁵ reported a convenient synthesis of cyclic (arylene disulfide) oligomers from dihydroxy starting materials as described in the following scheme.



Scheme 1.6 Synthetic route to cyclic oligomeric (arylene disulfide)s

Takekoshi et al^{16,17} described the synthesis of macrocyclic oligoether imides by reacting equimolar quantities of bis (trimethyl silyl ether) of bisphenol and arylene bis(fluorophthalimide), under high dilution conditions.



Scheme 1.7 Synthetic route to cyclic oligo(ether imide)s

All these new classes of oligomeric cyclic precursors exhibit low melt viscosities and therefore can be easily melt processable by using techniques such as reaction injection molding, compression molding, etc..

1.4. Cross-linkable low molecular weight linear oligomers

One of the examples of this class of materials is oligomeric polyimides end-capped with reactive norbornene or acetylenic moieties.¹⁸⁻²²



Figure 1.3 Oligoimides with cross-linkable moieties

Because these materials are low molecular weight they have comparatively low melt viscosities and can be easily processed and then cross-linked at a later stage in the mold.

The oligomeric cyclic precursors that were discussed in the previous sections, give thermoplastics via ring-opening polymerization. However, if oligomeric polycyclic materials are synthesized, then several cyclics may ring-open simultaneously resulting in a thermoset material rather than a thermoplastic.

In order to synthesize polycyclic materials we first prepared some oligomeric phenol-formaldehyde resins. The historical development and some basics of phenolformaldehyde resins will be discussed in the following sections.

1.5. Phenol-Formaldehyde resins

Johann Friedrich Wilhelm Adolph Von Baeyer²³⁻²⁵, one of the great organic chemists of the nineteenth century, was the first to report the results of mixing aldehydes and phenols in the presence of strong acids in the year 1872. He discovered that this reaction produced an unmanageable resinous mass and he could not obtain any pure materials from these reactions. The analytical tools were so primitive at the time that it was next to impossible to characterize these materials. There were a few other reports of work in this area which failed to produce any useful commercial materials.²⁶ Leo Hendrik

Baekeland was the key innovator in the commercialization of phenol-formaldehyde resins, also referred to as Bakelite resins. He established the important differences between the acid- and alkali-catalysed products obtained from phenol and formaldehyde as starting materials.²⁷ He also established the importance of excess phenol or formaldehyde in the production of these resins. Two patents issued to Baekeland ²⁸⁻²⁹ in the year 1909 laid the foundations of the phenolic resin industry. The Bakelite process, described in over 400 patents issued to Baekeland, formed the basis for the first large-scale production of a synthetic plastic.³⁰ Phenol-formaldehyde resins are classified as novolac and resole resins that are described below.

1.5.1. Novolacs

Novolac resins are produced by an acid catalysed reaction between phenol and formaldehyde. Less than one mole of formaldehyde is used per mole of phenol. The acid catalysts frequently used are sulfuric acid, p-toluenesulfonic acid, and oxalic acid. The mechanism of formation of ortho-substituted resins is described in the following scheme.³¹⁻³³



Scheme 1.8 Acid-catalysed condensation of phenol with formaldehyde

Similar reactions occur for p-substituted products. Meta-substitution is not observed under these conditions. Acid catalysis yields permanently stable, thermoplastic resin compositions which are converted to thermosetting materials by the use of a curing agent. Novolacs are generally marketed in the solid form.

1.5.2. Resoles

Resole type resins are produced by an alkaline catalysed reaction between phenol and formaldehyde. The ratio of formaldehyde to phenol varies from 1.2:1 to 3.0:1. Alkaline catalysts generally used for this reaction are NaOH, $Ca(OH)_2$, and $Ba(OH)_2$. Base catalysed reaction proceeds by a nucleophilic addition mechanism as follows.



Scheme 1.9 Base-catalysed condensation of phenol with formaldehyde

Resoles are inherently thermosetting in nature and no curing agent is needed to initiate cross-linking. The largest volume usage for resoles is in liquid form. They are sometimes mixed with novolacs to act as cross-linkers.

1.5.3. Substituted Phenols

Substituted phenols, e.g., cresol (o-, m-, p-), p-t-butylphenol, p-octylphenol etc., are similarly condensed with formaldehyde to produce specialty phenolic resins.^{27,34} High formaldehyde to phenol ratios can be used even for acid catalysed reactions with these substituted phenols. They find applications in areas such as coatings, adhesives etc.

1.5.4. Functionalization of novolacs

4-t-butylphenol-formaldehyde resin has been oxyalkylated by reacting with ethylene oxide and the product was marketed for use as demulsifiers.³⁰



Scheme 1.10 Synthetic route to oxyalkylated phenol-formaldehyde resins

Epoxy novolacs have also been synthesized by reacting novolacs with epichlorohydrin. They are used in molding applications.¹



Scheme 1.11 Synthetic route to epoxy novolacs

The functionalization of phenol-formaldehyde resins generates materials with interesting properties which continue to find commercial applications in many different arenas of polymer and materials science. With the advent of new and powerful characterization techniques, it makes it even more feasible to venture into the realm of new materials synthesis.

1.6. Matrix Assisted Laser Desorption Ionization - Time of Flight Mass Spectrometry (MALDI-TOF MS)

MALDI-TOF MS played a crucial role in the identification and characterization of the polycyclic structures that are being discussed in the following chapters of this thesis. A brief overview of this technique will be presented in the following sections.

MALDI-TOF MS is inherently a "soft" ionization technique which analyzes large delicate molecules without significant fragmentation. Michael Karas and Franz Hillenkamp coined the term "matrix assisted" for the first time in the year 1985. It was a major steppingstone in the area of mass spectrometry when they discovered in 1987 that the mass limitation of laser desorption could be overcome by mixing the sample with a "matrix" molecule which can absorb UV light.³⁵ In the same year Koichi Tanaka and coworkers at Shimadzu Corp., Kyoto, Japan, independently developed a similar technique. The Kompact MALDI III instrument which we used for this study, is manufactured by Shimadzu Scientific Instruments at the present time.

The operating principle underlying KOMPACT MALDI technique is quite simple. The sample solution under investigation is mixed with a specially selected matrix compound and it is then placed onto a sample slide. It is allowed to dry as a crystalline coating. The sample slide is then inserted into the instrument and kept under vacuum. A short pulse of laser light is directed onto a localized area of the sample causing sample molecules to desorb almost instantaneously. Desorption is a process in which a compound is released from a surface and ionized. A schematic illustrating sample ionization is presented in Figure 1.4.



Figure 1.4 Sample ionization in MALDI-TOF MS

1.6.1. Matrix

The desorption of the sample from the sample slide is greatly enhanced by the presence of a matrix. The matrix basically protects the sample molecules from direct contact with the laser pulse which can cause unwanted fragmentation. ³⁶ The criteria for the selection of a matrix is

- a) The matrix should absorb UV light at or near the wavelength at which the laser operates.
 In the Kompact MALDI instrument this wavelength is 337 nm.
- b) The matrix must be compatible with the sample under study i.e., it must form a homogeneous mixture with the sample.

Structures of a few common matrices are presented in figure 1.5.



Figure 1.5 Common matrices used in MALDI-TOF

1.6.2. Cationization agents

Generally metal ions such as Li⁺, Na⁺, K⁺, Ag⁺, etc., in the form of a salt solution, are used as cationization agents. In the analysis of polar materials the addition of cationization agents is not always necessary.³⁷ Choice of these cations are very much sample dependent. They are deliberately added to the solution of sample and matrix in order to enhance the resolution and signal to noise ratios. The best signals are obtained by the right combinations of sample, matrix and cationization agents.

1.6.3. Ion source

A typical ion source consists of a laser, focusing optics, an attenuator, a sample stage and an ion accelerator.

The laser used in Kompact MALDI III is a nitrogen laser that operates at 337 nm and uses a 3 ns pulse width to hit the sample surface. Focusing optics help in focusing the laser light onto a very localized area of the sample which causes it to vaporize rapidly. An attenuator generally regulates the amount of energy that reaches the analyte. The sample stage is a probe on which the sample slide is mounted. The function of the ion accelerator is to pull the desorbed ionized molecules into the gas phase and into the mass analyzer by using an applied electric field.

1.6.4. MALDI-TOF configurations

Time of flight mass spectrometry operates on the principle that the lighter ions travel faster than the heavier ions and thus reach the detector before the similarly charged heavier ions. In MALDI-TOF MS instruments, the mass analysis is primarily done by using two different analyzer modes, namely linear and reflectron modes.

In the linear mode the flight path travelled by the ionized samples is linear and shorter. Analytes of molecular weights higher than 10, 000 Dalton (Da) are generally analyzed using the linear mode. It provides better sensitivity for the detection of higher molecular mass. However, the resolution in this mode is lower than the reflectron mode.

In the reflectron mode, on the other hand, the flight path is longer and hence the molecular ions travel longer before they reach the detector and get better separated. It is more suited to the analysis of molecules having mass range lower than 10, 000 Da.³⁷

1.6.5. Advantages of MALDI-TOF MS

It provides absolute determination of molecular weights with a very low sample quantity and short analysis time.³⁸ In addition, it is capable of detecting the mass of repeat units and end-groups of a polymeric or oligometric mixture. On the contrary, conventional techniques for molecular weight determinations of polymers like Gel Permeation Chromarography can only furnish estimated molecular weights and it requires much longer time for analysis. The potential of MALDI-TOF MS technique for the analysis of polymers and oligometric seems unlimited.
1.7. Strategy and goals

Our primary objective in this thesis was to synthesize thermosetting materials with interesting properties by thermal cross-linking of mixed polycyclic precursors with comparatively low melt viscosity. The development of these precursors are outlined in this section and in depth studies will be presented in the subsequent chapters of this thesis.

A convenient synthetic route was developed to synthesize p-substituted phenolformaldehyde novolac type resins. A detailed study for this development is presented in chapter 2. The phenolic groups of these oligomeric resins were then functionalized to generate three novel classes of polycyclic precursor resins.

BPA polycarbonate is an important engineering thermoplastic. To achieve a material that is a thermoset with properties of polycarbonate, P-F resins were functionalized with triphosgene to give polycyclic carbonate precursors. When these precursors were thermally cured in the presence of a catalyst, they gave a highly cross-linked carbonate network. The synthesis and cross-linking study of these polycyclic carbonates are described in chapter 3.

Phosphonates are known to be good flame retardant materials. In order to impart good flame retardant properties to phenol-formaldehyde resins, polycyclic phosphonates were synthesized and were subjected to ROP to give cross-linked phosphonates. The synthesis and property profiles of these materials are discussed in chapter 4.

Organosiloxanes are another class of materials with many useful properties. Our objective was to incorporate these properties of siloxanes into phenol-formaldehyde resins. Oligomeric polycyclic siloxane resins were prepared in high yield from the starting phenol-formaldehyde resins. The cross-linked polysiloxane resins were stable at elevated temperatures. Chapter 5 illustrates the preparation and thermal properties of this new class of polycyclic materials.

A novel Bisphenol A dimer was synthesized by a convenient one-step reaction to provide a tetrafunctional starting material. Again, three different types of aforementioned oligomeric polycyclics were synthesized from the BPA dimer. In addition, we synthesized some co-polymers from the dimer with internal cross-linkable cyclic moieties which could be ring-opened thermally to give thermosetting materials. The synthetic methods are described in detail in chapter 6.

Keeping in mind the importance of processability we also synthesized some low molecular weight metal/phthalocyanine end-capped poly(aryl ether sulfone)s. The stacking phenomenon of the metal/phthalocyanine rings was explored. The physical properties of these polymers, before and after end-capping with metal/phthalocyanine rings were studied in detail as described in chapter 7.

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Chapter 2. Synthesis and Characterization of p-Substituted Phenol-Formaldehyde Novolac Type Resin

2.1 Introduction

Phenolic resins, considered to be the first synthetic polymers, are still a substantial business after eight decades.¹⁻⁴ These resins are prepared by the reaction of a phenol or a substituted phenol with formaldehyde under acidic or basic conditions. Acid catalyzed condensation of phenols with formaldehyde results in the formation of soluble, amorphous novolac resins.

The reaction of phenol with an aldehyde was first reported by Baeyer in 1872.⁵ However, the innovative work of Baekeland in 1909,⁶ serves as the foundation of phenolformaldehyde chemistry. 4-Alkylsubstituted phenolic resins are generally being used in applications such as coatings,⁷ adhesives,⁸⁹ and as molding compounds.

Traditionally GC,¹⁰ HPLC,^{11,12} GPC¹³ and NMR¹⁴⁻¹⁸ have been used to elucidate the structures of phenol-formaldehyde resins. They have been very useful in revealing the average molecular weights, sizes and distribution of different phenolic resins. None of these techniques, however, gives a precise description of the polymer nor do they provide an end-group analysis. Matrix Assisted Laser Desorption / Ionization-Time of Flight Mass Spectrometry (MALDI-TOF MS) is a soft ionization technique developed by Karas and Hillenkamp¹⁹ and is now an established technique for the analysis of large biopolymers.²⁰ ²² MALDI has also been found to be an invaluable tool for the characterization of synthetic polymers.²³ This method is very distinct from the other molecular weight determination techniques such as GPC, HPLC etc. since it can provide absolute molecular masses for each oligomeric species as well as furnishing information about the end groups.

2.2. Strategy and goals

In this chapter we will discuss the analysis of p-substituted phenol formaldehyde oligomers and the applicability of MALDI-TOF MS technique to the characterization of these oligomers with special emphasis on end group analysis. The use of MALDI-TOF MS for the analysis of phenol-formaldehyde resins has been recently reported.²⁴

2.3. Synthesis of p-substituted phenol-formaldehyde resins

Two synthetic methodologies were employed in the preparation of p-substituted phenol-formaldehyde resins. In both cases a 37% solution of formaldehyde in methanol and water was used. Sulfuric acid was used as a catalyst in one method while the catalyst was a cation-exchange resin in the other case. Xylene, used as an azeotropic solvent in method A was replaced by chlorobenzene in method B.

2.4. Characterizations of p-substituted phenol-formaldehyde resins

The MALDI-TOF spectrum of the 4-tert-butylphenol-formaldehyde resin that resulted by following the literature procedure²⁵ is shown in Figure 2.1. It clearly demonstrates the presence of two series of oligomers where n ranges from 2 to 14. A peak with a mass difference of 44 appears between the expected oligomeric species. For example, the peak at 643 Dalton (Da) represents a linear 4-tert-butylphenol-formaldehyde tetramer with the attachment of a lithium cation. The peak at 599 Da, however, corresponds to a phenol-formaldehyde trimer end-capped by one xylene molecule with a lithium cation attached to it. This combination of peaks repeats itself throughout the entire range of the mass spectrum for the oligomers prepared by the literature method.

The presence of xylene moieties in the polymer can be confirmed by NMR. The split multiplet at 2.2 ppm in the ¹H NMR spectrum (Figure 2.2) is due to CH_3 protons of xylene end-capper present in the oligomeric clusters. This multiplet disappears when xylene is not used as solvent as is shown in Figure 2.8.



Figure 2.1. MALDI-TOF spectrum of 4-tert-butylphenol-formaldehyde oligomers endcapped with xylene

Under the same reaction conditions 4-phenylphenol was reacted with formaldehyde using xylene as a solvent. In this case if incorporation of xylene occurred we would expect a mass difference of 64 Da instead of 44 Da. The MALDI-TOF spectrum (Figure 2.3) does in fact show the additional peaks with a mass difference of 64 Da for 4phenylphenol-formaldehyde oligomers. By changing the catalyst from sulfuric to hydrochloric acid and changing the reaction temperatures, similar MALDI-TOF spectra were obtained i.e., in each case xylene end-capped oligomers were observed. When oxalic acid, a mild acid, which is being widely used for the production of novolac resins, was used, there was no sign of xylene end-capped oligomers in the mass spectrum. However, only very low molecular weight oligomers were obtained under these conditions.



Figure 2.2. ¹H NMR spectrum of 4-tert-butylphenol-formaldehyde oligomers end-capped with xylene in DMSO-d₆

The reaction between a phenol or a substituted phenol and formaldehyde under strongly acidic conditions, takes place by an electrophilic aromatic substitution mechanism. Benzylic carbocations that are formed under acidic conditions, react very rapidly with phenol (Scheme 2.1) to give methylene bridged dimer.²⁶ In the presence of xylene, however, the benzylic carbocation of the n-mer could presumably react with a xylene molecule in addition to reacting with another phenolic moiety, to yield end-capped xylene oligomers. Probably the electron donating nature of the methyl groups in xylene make it susceptible to attack by benzylic carbocations.



Figure 2.3. MALDI-TOF spectrum of 4-phenylphenol-formaldehyde oligomers endcapped with xylene

To avoid the incorporation of xylene we used an alternate route for the synthesis of the phenol-formaldehyde resins (Scheme 2.2). Xylene was replaced by chlorobenzene and and a cation-exchange resin (Amberlyst-15) was used as catalyst.





Scheme 2.1. Mechanism of formation of xylene end-capped phenol-formaldehyde resin



 $R = C_4 H_9, C_6 H_5$ etc.

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Scheme 2.2. Synthesis of p-substituted phenol-formaldehyde oligomers by using cationexchange resin as a catalyst



Figure 2.4. MALDI-TOF spectrum of 4-tert-butylphenol-formaldehyde oligomers (P/F=1/0.3)

The advantage of using a cation-exchange resin is that it is reusable for long period of time and the products are separated by a simple filtration. Figures 2.4 and 2.5 show the MALDI-TOF spectra of different oligomeric resins with variable P/F ratios. There is no trace of any side products visible in these spectra. Proton NMR spectra also give no indication of any side products. HPLC and GPC in Figures 2.6 and 2.7 respectively are complementary to those of MALDI-TOF.



Figure 2.5. MALDI-TOF spectrum of 4-tert-butylphenol-formaldehyde oligomers (P/F=1/0.8)

P-F resins have already been studied extensively by NMR spectroscopy.¹⁴⁻¹⁸ Figure 2.8 represents the NMR analysis of a 4-tert-butylphenol-formaldehyde oligomers obtained by using CDCl₃ as a solvent. In addition to the OH proton peaks in the region of 4.4-5.6 ppm, there were also some other OH peaks in the range 8-10 ppm. This is attributed to H-bonding between the OH groups of the phenolic resins. The phenomena of H-bonding in the P-F resins has been observed before.²⁷ When the polymer solution in CDCl₃was treated with D₂O, the intensity of the peaks in the aforementioned region was dramatically reduced. This provides a direct evidence of H-bonding in these resins.



Figure 2.6. Gradient HPLC traces of 4-tert-butylphenol-formaldehyde oligomers



Figure 2.7. GPC traces of 4-tert-butylphenol-formaldehyde oligomers



Figure 2.8. ¹H NMR spectrum of 4-t-butylphenol-formaldehyde resin

2.5. Conclusions

MALDI-TOF analysis has been found to be very valuable in characterizing the xylene end-capped p-substituted phenol-formaldehyde oligomers. Synthesis using cation-exchange resin as catalyst gave p-substituted phenol-formaldehyde oligomers without any undesired side products.

2.6. Experimental Section

Materials

Sulfuric acid (ACP; 95-98%), hydrochloric acid (ACP; 36.5%), xylenes (Caledon; 98.5%), chlorobenzene (ACP), formaldehyde (BDH; 36.5-38%), Amberlyst-15 (BDH), 4phenylphenol (Aldrich; 97%) were used without further purification. 4-tert-Butylphenol (Aldrich; 99%) was recrystallized from hexanes prior to use.

Matrix Assisted Laser Desorption/Ionization-Time of flight mass spectrometry

All samples were analyzed using a Kratos Kompact MALDI-III TOF bench top model. It generates a maximum laser output of 6 mw at a wavelength of 337 nm (N_2 laser light, 3ns pulsewidth). The average of 100 laser shots was represented in the mass spectra.

The MALDI-TOF instrument has the capability of analyzing samples in both linear and reflectron modes. All samples for this paper were analyzed by using the reflectron mode to obtain higher mass resolution. Insulin (for low molecular weight polymers) and bovine serum albumin (for high molecular weight polymers) were used for an external mass calibration.

Sample preparation for MALDI-TOF

All the samples (5 mg/mL) and dithranol (10 mg/mL) were prepared in chloroform solution. LiBr (5 mg/mL) was dissolved in THF. The solutions were combined in 1:2:1 volume ratio of polymer to matrix to cationization agent. 0.1 μ L of the mixture was applied

to a spot on a sample slide and the solvent was allowed to evaporate slowly before being put into the vacuum chamber of the mass spectrometer.

Characterization of the resins using other techniques

HPLC analyses of the 4-alkylsubstituted phenol-formaldehyde (P-F) oligomers were carried out on a Milton Roy CM4000 pump equipped with a reverse phase column (prime sphere 5μ C8, 250x4.6 mm) and a UV detector at 300 nm. A mixture of THF and water was used as an eluent. The gradient program was as follows: Step1, 70-95% THF over 20 min; Step2, 95-100% THF over 5 min; Step3, 100-70% THF over 5 min; (recycle).

All the GPC analyses were performed on a Waters 510 HPLC using four phenogel 5 μ m columns (1 linear, 3x500 Å) arranged in series. Spectroscopic grade chloroform was used as an eluent with a flow rate of 1mL/min. The UV detector was set at 254 nm and polystyrene was used as external calibrant. NMR spectra were recorded on a Varian Unity 500 instrument using DMSO-d₆ or CDCl₃ as solvent.

Synthesis of 4-alkyl substituted phenol-formaldehyde oligomers

Method A

The synthesis of 4-alkyl substituted phenol-formaldehyde oligomers was performed following a literature procedure.²⁵ A 250 mL three neck round-bottom flask was equipped with a Dean-Stark trap, a condenser, a volumetric addition funnel, and a nitrogen inlet and it was charged with 4-tert-butylphenol (8 g, 53 mmol) and 105 mL of xylene. The phenol went into solution at 30 °C. After the addition of sulfuric acid (0.28 mL) the temperature of the reaction mixture was increased to 80 °C. The formaldehyde solution (36.5-38%) was added to the reaction mixture dropwise over a period of 30 min. After the addition was complete the temperature of the mixture was raised to 120 °C and the water began to be removed as an azeotrope. The mixture was stirred at this temperature for 4 hrs. Xylene was removed under reduced pressure and the solid residue was dissolved in chloroform which was then washed with 0.1M aqueous solution of potassium bicarbonate to neutralize

the acid catalyst. The organic layer was extracted and chloroform was removed under reduced pressure to give 85-90% yield of a white colored resin.

Method B

A 500 mL 3-neck round-bottom flask fitted with a reflux condenser and a nitrogen inlet was charged with 4-tert-butylphenol (50 g, 0.33 mol), (37%) formaldehyde solution, Amberlyst-15 (20 g, 40 wt %) and chlorobenzene (50 mL). For each mole of 4-tert-butylphenol, 0.3-0.8 mole of formaldehyde solution was added. For example, for 50 g of 4-tert-butylphenol, 20 mL solution of formaldehyde was used to obtain a P/F ratio of 1/0.8. The reaction mixture was heated to 100 $^{\circ}$ C and stirred continuously at this temperature for 4 hours. The resin was then filtered off and the filtrate contained the oligomeric product in chlorobenzene. Chlorobenzene was removed under reduced pressure and the oligomers were vacuum dried at room temperature to give ~90% yield of a white resin.

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Chapter 3. Polycyclic Carbonates: Novel Precursors for Thermosetting Resins

3.1 Introduction

Prochaska¹⁻⁵ pioneered the synthesis of aromatic cyclic carbonates and their conversion to high molecular weight polymers via ring-opening polymerization (ROP) about two decades ago. Prochaska demonstrated that o,o'-biphenols and bis(2-hydroxyphenyl)methanes readily form cyclic carbonates (Scheme 3.1) when reacted with phosgene in the presence of a base. He further demonstrated that these cyclic materials would undergo a ring-opening polymerization at elevated temperatures in the presence of a catalytic amount of potassium carbonate and that this reaction was reversible since cyclics could be formed from the polymers at elevated temperatures under reduced pressure.

Commercial polycarbonates are generally linear polymers. The rheological properties can be modified and the melt strength can be increased significantly with the introduction of branching into the polymer backbone. More recently, Rosenquist et al ⁶⁻⁸ synthesized some novel bis(cyclic carbonates) to introduce branching into linear polycarbonates.

By the enzymatic oxidation of 4-substituted phenols, polymers (o,o'-coupled) can be readily obtained and they have recently been commercialized. ¹⁰⁻¹² We initially reacted these biphenols with triphosgene in an attempt to form polycyclic structures (Scheme 3.1). However, because of steric reasons the functionalization was not complete and a large amount of residual hydroxy groups remained. These results led us to synthesize low molecular weight novolac resins from 4-alkyl substituted phenols. The dimer content in the starting phenol-formaldehyde resin was minimized in order to avoid the formation of linear polymer segments after the ring-opening polymerization. With a suitable initiator, the polycyclic carbonates should ring-open to give highly cross-linked networks.



R= -H, -CH₃, -Cl, -OCH₃ etc. X= -, CH₂, C(CH₃)₂, -O-, -C(C₂H₅)₂, etc.



R₁ = aikyi, aryi, haloaikyi, aliyi etc.

Scheme 3.1. Synthesis of polycyclic carbonates from 0,0' polyphenols

MALDI-TOF analysis was used for the detection of the absolute masses of the different functionalized polycyclic carbonate resins.

3.2 Strategy and goals

Our goal in this chapter is to demonstrate the synthesis of polycyclic carbonates with maximum functionalization of the OH moieties, to characterize the functionalized resins and cross-link them to obtain thermosetting materials with improved physical and mechanical properties.

3.3 Synthesis of phenolic resins

The low molecular weight C-C coupled 4-t-butylphenol oligomers (M_n =530 g/mol) used in this study which were obtained from Enzymol International Inc., were prepared by enzymatic oxidation of phenols.¹⁰⁻¹² The 4-alkyl substituted phenol-formaldehyde oligomers were prepared by reacting the substituted phenol with formaldehyde in a 1/0.85 molar ratio. The reactions were carried out in chlorobenzene with a cation-exchange resin as catalyst by following the procedure previously described in chapter 2.⁹ The product yields were 90-95 %.

3.4. Characterization by MALDI-TOF MS

Recently, MALDI-TOF characterization of some commercial oligomeric BPAcarbonates has been reported.¹³ It has also been documented that the addition of metal salts to the matrix-polymer mixture enhances the ionization.^{14,15} In the case of the polycyclic carbonate resins we used LiBr as a cationization agent.

The MALDI-TOF spectrum of low molecular weight phenolic resins from Enzymol is presented in Figure 3.1.



Figure 3.1. MALDI-TOF spectrum of 4-t-butylphenol resin

The number of repeat units ranges from 2 to 9. The MALDI-TOF spectrum of the polycyclic carbonate of this resin is shown in Figure 3.2. The intense signal at 626 Dalton (Da) is that of a tetrameric phenol containing one carbonate ring with a lithium ion attached to it. The signal at 651 Da represents a species with two cyclic carbonate moieties derived from a tetramer. The mass at 800 Da represents a pentameric phenol with two carbonate rings and a free phenolic moiety whereas the one at 773 Da represents a pentamer with only one carbonate ring and three residual phenolic groups. The maximum number of carbonate rings observed is three which shows up at mass 974 Da. The relevant structures with their masses are shown in Scheme 3.2.



Figure 3.2. MALDI-TOF spectrum of the polycyclic carbonates of 4-t-butylphenol resin

It becomes increasingly difficult to ring close the phenolic groups to carbonates as the molecular weight of the phenolic resin increases. An increasing number of residual

phenolic groups that are not functionalized remain as the mass increases as is apparent from the spectrum in Figure 3.2. In addition, no intermolecular condensation product was observed in MALDI spectra. We therefore turned our attention to the 4-alkyl substituted phenol-formaldehyde oligomers which should have less steric hindrance to ring formation because of the presence of the methylene bridges.



Scheme 3.2. Proposed structures of polycyclic carbonates of 4-t-butylphenol resin

Figure 3.3 represents the MALDI-TOF MS of polycyclic carbonates of 4-tbutylphenol-formaldehyde resin. Each mass species in the spectrum is attached to a lithium cation. The mass at 694 Da corresponds to an oligomer with two carbonate rings in the structure (structure A, Scheme 3.3). The intense peak at mass 856 Da is due to a bicyclic carbonate with one free phenolic group and an attached lithium cation (structure B1, Scheme 3.3). Minimized molecular models for the two isomers corresponding to mass 850 are presented in Figure 3.4. We would expect that the terminal hydroxy groups would most likely first ring close to give cyclic carbonates or react intermolecularly with odd numbered species.



Figure 3.3. MALDI-TOF spectrum of the polycyclic carbonates of 4-t-butylphenolformaldehyde resin

Residual hydroxy groups toward the middle of the chain are sterically hindered and in oligomers with odd number of phenolic groups, the remaining unreacted phenolic group is too hindered to react intermolecularly to form carbonates. The mass at 845 Da could be due

to the structure B2 of Scheme 3.3. This type of intermolecular reaction is possible because of the presence of some free 4-t-butylphenol monomer. The signal at mass 1045 Da corresponds to a resin with three carbonate rings (structure C1, Scheme 3.3). The mass at 1033 Da corresponds to a hexamer with two carbonate rings (structure C2, Scheme 3.3). The formation of this type of species is possible by the intermolecular reaction of two trimers each containing one carbonate ring and a free phenolic group. One of the possible structures for mass 1020 Da is shown in Scheme 3.3 (structure C3). The mass at 1007 Da is possibly due to structure C4 (Scheme 3.3). The additional peaks in each set of oligomeric clusters are presumably due to intermolecular reactions between two different nmers or between an n-mer and a monomer. 4-t-butylphenol-formaldehyde resin containing up to five carbonate rings corresponding to mass 1746 Da are detectable in the MALDI-TOF spectrum.



Figure 3.4. Molecular models of the two isomers of a carbonate resin with two carbonate rings

The MALDI-TOF spectrum of 4-phenylphenol-formaldehyde resin before functionalization to a carbonate is shown in Figure 3.5. Figure 3.6 is the MALDI-TOF spectrum for the corresponding polycyclic carbonates of this 4-phenylphenol-formaldehyde resin. Ten different ion clusters are visible. In this case the lowest mass at 564 Da (structure A, Scheme 3.4) is a trimer with one carbonate ring. The strongest signal is observed at mass 772 Da (structure B, Scheme 3.4) which is presumably due to a tetramer with two cyclic carbonates. The mass at 1161 Da (structure C1, Scheme 3.4) represents a hexameric species with three carbonate rings. One of the possible structures for mass at 1149 Da is presented in Scheme 3.4 (structure C2). This is again due to an intermolecular reaction between two trimers. The possible structures for masses at 1134 Da (structure C3) and at 1122 Da (structure C4) are also shown in Scheme 3.4. The molecular ions do not appear as adducts of lithium ions in this case. The percent error between the calculated and observed mass varies from 0.1 % to 0.2 %.



Scheme 3.3. Proposed structures of the polycyclic carbonates of 4-t-butylphenolformaldehyde resin



Figure 3.5. MALDI-TOF spectrum of 4-phenylphenol-formaldehyde resin



Figure 3.6. MALDI-TOF spectrum of the polycyclic carbonates of 4-phenylphenolformaldehyde resin



Scheme 3.4. Proposed structures of the polycyclic carbonates of 4-phenylphenolformaldehyde resin

3.5. Characterization by NMR

From the MALDI-TOF analysis it is quite clear that the amount of residual phenolic groups in these cyclic systems is very low. This is also evident in the ¹H NMR spectrum (Figure 3.7) of these carbonate resins. The phenolic protons appear between 8 and 10 ppm in the ¹H NMR spectrum when taken in DMSO-d₆ solvent. The aromatic region (6-7.6

ppm) also shows a very complex multiplet because of the oligomeric nature of the polycyclic resins. The conversion of the majority of phenolic groups to cyclic carbonates is confirmed by the ¹³C NMR spectrum (Figure 3.8).

It has been reported earlier that the carbonyl carbons for cyclic oligomeric carbonates appear at around 150 ppm in the ¹³C NMR spectra.¹⁶ The appearance of several peaks at around 150 ppm is an indication of the presence of different carbonyl carbons. The number of quaternary carbons directly attached to hydroxyl groups are very low (between 150 and 160 ppm) again implying the presence of a very low level of -OH groups in the polycyclic carbonate resins.



Figure 3.7. ¹H NMR spectrum of the polycyclic carbonates of 4-t-butylphenolformaldehyde resin



Figure 3.8. ¹³C NMR of the polycyclic carbonates of 4-t-butyl P-F resin

3.6. Characterization by Gradient HPLC

A gradient HPLC chart of the cyclic carbonate resins is presented in Figure 3.9. The broad peaks in this chart are probably due to the oligomeric clusters observed in the respective MALDI-TOF spectrum (Figure 3.6). Furthermore, it is also quite obvious from the HPLC chart that there are no higher molecular weight polymeric species present in these carbonate resins.



Figure 3.9. A gradient HPLC trace of the polycyclic carbonate of 4-phenylphenolformaldehyde resin

3.7. Cross-linking study of the polycyclic carbonates

Cross-linking studies on these polycyclic carbonate resins were carried out in order to evaluate the feasibility of utilizing them as thermosetting materials. Lithium stearate (LIST) has been found to be one of the better transesterification catalysts for the crosslinking of polycarbonates in the ring-opening polymerization of cyclic carbonates. ⁶⁻⁸ The glass transition temperature of the polycyclic carbonate of 4-t-butylphenol-formaldehyde resin is around 110 °C. When the cyclic carbonate resin was cured with 1 mol % of LIST at 300 °C for 30 minutes, the glass transition temperature increased to 180 °C. However, when the resin was cured at 350 °C for 30 minutes no glass transition temperature was observed, indicating the formation of a highly cross-linked network. Similar behavior was subjected to curing under the same conditions. The polycyclics were also mixed with commercial linear polycarbonates in different proportions before curing. A typical DSC scan for the curing of 10 wt % polycyclic carbonate of 4-t-butylphenol-formaldehyde resin in a commercial polycarbonate at two different temperatures is presented in Figure 3.10.



Figure 3.10. DSC scans for the curing of 10 wt % polycyclic carbonate of 4-tbutylphenol-formaldehyde resin in a commercial Bisphenol A polycarbonate mixture

The glass transition temperature (T_g) of the commercial linear polycarbonate is 150 °C. It was found that curing a mixture of 10 wt % polycyclic carbonate resin in linear polycarbonate at 300 °C for 30 minutes the T_g remains at 150 °C which indicates the presence of relatively few cross-links in the sample. However, after curing at 350 °C for 15 minutes the T_g of the linear polycarbonate increased from 150 °C to 176 °C. When the curing was conducted at 350 °C for 30 minutes for the same mixture no T_g was detected. The T_g values for different concentrations of polycyclic carbonate resin in the linear carbonate is presented in Table 3.1.

% Polycyclic	Tg(°C)	Curing	Curing
carbonate resin		temp.(°C)	time(min.)
10	150	300	30
10	154	300	60
10	176	350	15
10	none	350	30
20	158	300	30
30	158	300	30
40	158	300	30

Table 3.1. T_g s of cured mixtures of a BPA polycarbonate with a polycyclic carbonate

It is quite clear that by increasing the amount of the polycyclic carbonates in BPA polycarbonate, the T_g does not increase much when the samples are cured at 300 °C. A similar study was conducted for the polycyclic carbonate of 4-phenylphenol-formaldehyde resin. In this case also, when cured at 350 °C for 15 minutes with 10 wt % polycyclic carbonate resin added, an increase of 30 °C in T_g was observed. When the same material was cured at 350 °C for 30 minutes no T_g was observed. The cured materials in both cases were insoluble in chloroform.

3.8. Conclusions

Efficient functionalization of the phenolic groups to form polycyclic carbonates of C-C coupled 4-t-butylphenol resins prepared by enzymatic oxidation, was not possible.

This was due to steric hindrance to ring closure in these systems. As a consequence these systems contained large amounts of residual hydroxy groups. In order to alleviate this problem, polycyclic carbonates were synthesized from 4-alkyl substituted phenol-formaldehyde resins by using solid triphosgene under high dilution conditions. Very few residual phenolic groups remained after functionalization in these systems. MALDI-TOF has been very useful in the characterization of these carbonate resins. A highly cross-linked thermosetting material was obtained when these resins were cured with a commercial polycarbonate by using lithium stearate as a catalyst.

3.9. Experimental section

Materials.

Chlorobenzene (ACP), formaldehyde (BDH; 36.5-38 %), Amberlyst-15 (BDH), triphosgene (Aldrich; 98 %), 4-phenylphenol (Aldrich; 97 %) were used as received. 4-t-Butylphenol (Aldrich; 99 %) was recrystallized from hexanes. Tetrahydrofuran (Aldrich; 99+%) and pyridine (Caledon; 99%) were distilled and dried before use. Commercial BPA polycarbonate (M_w =33,000) and resins obtained by the enzymatic oxidation of 4-t-butylphenol were kindly supplied by General Electric and Enzymol International Inc., respectively.

Techniques used for characterization

A Kratos Kompact MALDI-III TOF mass spectrometer was used for mass analysis. A maximum laser output of 6 mw is generated at a wavelength of 337 nm (N_2 laser light, 3 ns pulsewidth). Each mass spectrum represents an average of 100 laser shots. The reflectron mode was used to analyze the samples for better resolution.

Dithranol was used as a matrix and LiBr as a cationization agent for all the samples. Dithranol (10 mg/mL) and LiBr (5 mg/mL) were freshly prepared in chloroform and THF respectively. The samples (5 mg/mL) were prepared in chloroform. A 1:2:1 volume ratio of polymer to matrix to cationization agent was used. A Varian Unity 500 instrument was used to obtain the nmr spectra. Thermal analyses of the polycyclic carbonate resins were carried out using a Seiko 220 DSC and a 220 TG/DTA instruments under nitrogen at a heating rate of 20 $^{\circ}$ C/min. Gradient HPLC was performed on a Milton Roy CM4000 pump equipped with a reverse phase column (prime sphere 5µ C8, 250x4.6 mm) and a UV detector at 254 nm. A mixture of THF and water was used as the mobile phase. The gradient program was as follows: step 1, 60-85 % THF over 20 min; step 2, 85-100 % THF over 5 min; step 3, 100-60 % THF over 5 min; (recycle).

General procedure for the synthesis of polycyclic carbonate resins from 4- alkylsubstituted phenol-formaldehyde oligomers

A 100 mL 3-neck round-bottom flask fitted with a reflux condenser and a nitrogen inlet was charged with pyridine (2.6 mL, excess) and dry THF (25 mL). The temperature of the flask was maintained at 50 °C. A mixture of 4-t-butylphenol-formaldehyde resin (2 g) and triphosgene (1.6 g, excess) in dry THF (15 mL) was added slowly to the reaction mixture over 3-4 h. The reaction mixture was stirred for another 5-6 h. The final concentration of the resin was about 0.25M. The white precipitate of pyridine.HCl was filtered off and the filtrate rotavapped to remove THF. The solid residue was dissolved in CHCl₃, washed once with 10 % HCl and three times with water. The CHCl₃ layer was then separated and rotavapped to dryness to give a white polycyclic carbonate resin. The yield of the final polycyclic carbonate resin was about 45 %.

Preparation of polycyclic carbonate resin samples for curing studies

The polycyclic carbonate resins were mixed with commercial polycarbonate (M_w =33,000) in different proportions and were prepared in a methylene chloride solution. To each solution, 1 mol % lithium stearate (based on the weight of linear polycarbonate) was added. The solvent was then evaporated and the samples were vacuum dried at 80 °C for about 16 h prior to conducting ROP. Curing studies were carried out in the TG/DTA instrument at different temperatures under nitrogen atmosphere.
3.10. References and notes

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Chapter 4. Polycyclic Phosphonate Resins: Thermally Crosslinkable Intermediates for Flame Retardant Materials

4.1. Introduction

It is well established that incorporation of phosphorus containing compounds into polymers improves their flame retardant properties.¹ Many flame retardant plastics have been prepared by the addition of phosphorus containing additives or the incorporation of phosphorus compounds into the polymer structure.²⁻⁵

BPA polycarbonates are one of the most important of the engineering thermoplastics and many efforts have been made in the past to increase the flame retardant properties of these materials. Additives like sodium 2,4,5-trichlorobenzene sulfonates are being used to improve the flame retardancy of polycarbonates.⁶ It has been reported in the literature that incorporation of phosphonate groups into polycarbonate improves their flame retardancy.⁷ Significant improvement in flame retardant properties of poly(carbonate-*co*-phosphonate)s was reported by Kim and co-workers.⁸ However, the thermal stabilities of these polymers decreased with the increase in phosphonate content. If the polyphosphonates were incorporated while cross-linking the polycarbonate backbone then presumably thermal stabilities as well as flame retardancy and solvent resistance would improve significantly.

Polyphosphonates are regarded as very good flame retardant materials.⁹ The synthesis of polyphosphonates by a solution polycondensation method has been documented.¹⁰ Tertiary amines have been used as catalysts to carry out the condensation reactions.^{11,12} Ring-opening polymerization of tri- and pentavalent cyclic phosphorus compounds are well known in the literature.^{13,14} In the present study, 4-substituted phenol-formaldehyde resins were reacted with phosphonic dichlorides under dilute condition in an

aprotic solvent to obtain polycyclic phosphonate resins. Under these conditions the species with even numbered hydroxy groups were completely substituted by phosphonic dichlorides to produce phosphonate containing rings in these systems. However, in the species with an odd number of hydroxy groups some intermolecular coupling occurred as well as having only one of the two chlorines in the phosphonic dichlorides react resulting in the formation of a small amount of residual P-Cl linkages. These linkages in the polycyclic systems upon hydrolysis gave acidic P-OH groups. The presence of acidic protons in these materials is highly undesirable because they can cause chain scission at elevated temperatures. In order to eliminate the acidic protons, the polycyclic phosphonate resins containing P-Cl linkages were reacted with a secondary amine which replaced all the P-Cl bonds by P-N bonds. The P-N linkages remained intact upon work-up. Transesterification reactions between the carbonate and phosphonate esters would be expected to be relatively easy.

4.2. Strategy and goals

Our goal in this chapter is to prepare novel polycyclic phosphonates from psubstituted phenol-formaldehyde resins which can be ring-opened to give thermosetting resins. In addition, we have attempted to impart flame retardant properties to commercial BPA polycarbonate by incorporating phosphonates as cross-links into the polycarbonates via transesterification reactions at elevated temperatures in the presence of a suitable initiator.

4.3. Synthesis of polycyclic phosphonates

Phenol and formaldehyde were used in 1/0.6 and 1/0.8 molar ratios to synthesize psubstituted phenol-formaldehyde oligomers in the presence of a cation-exchange resin in chlorobenzene as described by us previously in chapter 2.¹⁵ Two series of polycyclic phosphonates were synthesized, one containing methyl and the other with a phenyl moiety on the pentavalent phosphorus. The synthetic procedure is described in the experimental section.

4.4. Characterization by MALDI-TOF

Detection of the absolute masses of different species of polycyclic phosphonates was done with MALDI-TOF MS. Figure 4.1 is the MALDI-TOF spectrum of 4-tbutylphenol-formaldehyde resin before functionalization. The ratio of 4-t-butylphenol to formaldehyde was 1 to 0.6 in this case.



Figure 4.1. MALDI-TOF spectrum of 4-t-butylphenol-formaldehyde resin

The MALDI-TOF spectrum of the polycyclic methylphosphonate of 4-t-butylphenolformaldehyde resin is shown in Figure 4.2. The peak at mass 379 dalton (Da) is due to a dimer with one eight membered phosphonate ring (structure A, Scheme 4.1) plus a lithium ion. The peak at mass 764 Da represents a species containing two phosphonate rings plus a lithium ion (structure B, Scheme 4.1). The signal due to species containing three phosphonate rings appears at mass 1149 Da (structure C, Scheme 4.1). In addition to the signals representing cyclic rings in the resin, there are also some peaks due to species that are not completely cyclic. For example, the mass at 542 Da (structure D, Scheme 4.1) represents a trimer with one methylphosphonate ring and a free phenolic moiety. The small peak at mass 705 Da (structure E, Scheme 4.1) is most likely due to a tetrameric species with two free phenolic moieties that are not functionalized. The signal at mass 927 Da represents a pentamer containing two methylphosphonate rings and a free phenolic group, presumably in the middle of the chain (structure F, Scheme 4.1).



Figure 4.2. MALDI-TOF spectrum of the polycyclic methylphosphonate of 4-tbutylphenol-formaldehyde resin (before amine addition)

When a single free phenolic group reacts with $MeP(O)Cl_2$, it gives rise to a species with a -P-Cl moiety with mass 637 Da (structure G, Scheme 4.1). If the reaction was stopped at this point and the mixture worked-up, the -P-Cl linkage would be converted to -P-OH. The presence of this acidic proton can cause break down of polymer chains when the resin is heated at elevated temperature in the presence of a catalyst.



Scheme 4.1. Proposed structures of the polycyclic methylphosphonates of 4-tbutylphenol-formaldehyde resin (before amine addition)

In order to avoid the formation of any acidic protons in these systems, the mixtures containing small amounts of -P-Cl linkages were reacted with a secondary amine e.g. diethylamine. The MALDI spectrum (Figure 4.3) indicated the complete disappearance of the species containing P-Cl linkages and new peaks representing -P-N linkages appeared. For example, the mass at 675 Da (structure A, Scheme 4.2) represents a species with one



Figure 4.3. MALDI-TOF spectrum of polycyclic methylphosphonate of 4-t-butylphenolformaldehyde resin (after amine addition)

Similarly, the signal at mass 1060 Da represents a pentameric species with two methylphosphonate rings and one -P-N linkage (structure B, Scheme 4.2). The intensities of the signals containing -P-N linkages are comparatively higher than their -P-Cl containing counterparts. The masses corresponding to different peaks in Figure 4.3 are presented in Scheme 4.2.

The MALDI-TOF spectrum of the starting 4-phenylphenol-formaldehyde resin is presented in Figure 4.4. The molar ratio of 4-phenylphenol to formaldehyde was 1 to 0.8. When phenylphosphonic dichloride was reacted with 4-phenylphenol-formaldehyde resin, a MALDI spectrum similar to that in Figure 4.2 was obtained. The MALDI-TOF spectrum of the products obtained before the addition of excess diethylamine to the reaction mixture is presented in Figure 4.5. In this case, however, more signals are observed and n goes from 1 to 4, probably because of the higher masses of the starting phenol-formaldehyde resin. In addition, the intensities of the signals with free phenolic moieties are much smaller than the corresponding species containing -P-Cl linkages.



Scheme 4.2. Proposed structures of polycyclic methylphosphonate of 4-t-butylphenolformaldehyde resin (after amine addition)

This suggests, perhaps, that most of the oligomeric species containing free phenolic moieties reacted with phenyl phosphonic dichlorides. The molecular structures corresponding to different masses in Figure 4.5 are given in Scheme 4.3.



Figure 4.4. MALDI-TOF chart of 4-phenylphenol-formaldehyde resin



Figure 4.5. MALDI-TOF chart of polycyclic phenylphosphonate of 4-phenylphenolformaldehyde resin (before amine addition)

Figure 4.6 shows the MALDI-TOF spectrum of the polycyclic phenylphosphonate resin where all the -P-Cl linkages were substituted by -P-N linkages. The intense signal at mass 858 Da represents a trimeric species with one phosphonate ring and one -P-N bond. There is no signal observed at mass 821 Da representative of the corresponding species with -P-Cl bond. This is clearly an indication of the disappearance of all the species containing -P-Cl linkages. Similarly, the signal at mass 1343 Da represents a pentamer with two phenylphosphonate rings and one -P-N linkage. In both cases intermolecular reactions do not seem to occur, perhaps because of lower reactivities of the phosphonic dichlorides. The percent error between the calculated and observed masses is within the range of 0.1 to 0.2 %.



Figure 4.6. MALDI-TOF chart of polycyclic phenylphosphonate of 4-phenylphenolformaldehyde resin (after amine addition)



Scheme 4.3. Proposed structures of polycyclic phenylphosphosphonate of 4phenylphenol-formaldehyde resin

4.5. Characterization by Gradient HPLC

The HPLC chart of this polycyclic phenylphosphonate is presented in Figure 4.7. It is quite clear from the HPLC chart that there is no high molecular weight material present in this resin.



Figure 4.7. Gradient HPLC chart of polycyclic phenylphosphonate of 4-phenylphenolformaldehyde resin (after amine addition)

4.6. Characterization by NMR

The ¹H NMR spectrum of the polycyclic phosphonates of 4-phenylphenolformaldehyde resin is presented in Figure 4.8. Methyl protons of the $(CH_3CH_2)_2N$ -P linkages show up as a mixture of split multiplets ranging from 0.6 to 1.4 ppm whereas the -CH₂ protons appear between 2.8 and 3.8 ppm. The appearance of these signals complements the peaks assigned to the species containing -P-N linkages in MALDI-TOF spectra presented in Figures 4.3 and 4.6. The methylene bridged protons appear as broad multiplets between 4 and 5 ppm. The aromatic protons appear as complex multiplets between 7.2 and 8.6 ppm. The ³¹P NMR is shown in Figure 4.9. The ³¹P nuclei appear as three different sets of signals in the spectrum. Multiple peaks around 12 ppm are due to different PhP(O) phosphorus groups attached directly to the eight-membered rings in the polycyclic systems. The ³¹P nuclei attached to Et_2N appear between 14 and 25 ppm. The mixture of singlets is most probably due to different electronic environments experienced by ³¹P nuclei. Similar types of ¹H and ³¹P spectra were obtained for the polycyclic



Figure 4.8. ¹H NMR spectrum of polycyclic phenylphosphonate of 4-phenylphenolformaldehyde resin in DMSO- d_{δ}



Figure 4.9. ³¹P NMR chart of polycyclic phenylphosphonate of 4-phenylphenolformaldehyde resin



Figure 4.10. ³¹P NMR spectrum of polycyclic methylphosphonate of 4-t-butylphenolformaldehyde resin

methylphosphonates of 4-t-butylphenol-formaldehyde resins. The ³¹P NMR of the polycyclic methylphosphonates is shown in Figure 4.10. The shielding effect of the

phenyl groups attached to ³¹P nuclei is quite apparent from these results since in this case, the signals due to different ³¹P nuclei appeared more upfield.

4.7. Cross-linking study

Curing studies were conducted at 350 °C for different time periods by incorporating various proportions of polycyclic phosphonates into commercial linear polycarbonate. This was done in order to obtain a thermosetting material containing phosphorus and to evaluate the flame retardancy of the phosphonate containing resins when cross-linked. The glass transition temperature (T_g) of the commercial polycarbonate is 150 °C. When the linear polycarbonate containing different amounts of polycyclic phenylphosphonates was cured at 350 °C for 30 minutes, the T_g value increased up to 200 °C. The glass transition temperatures did not increase steadily with the increase in phosphonate contents in polycarbonates when the materials were cured under similar conditions. When the curing was done at 350 °C for one hour, no glass transition temperature was detected implying the formation of highly cross-linked systems.

4.8. Flame retardance study

One way to estimate the flame retardancy of phosphonate containing materials is to obtain percent char yield. When the materials are heated at very high temperatures, as in a fire, the phosphorus containing groups decompose to form a phosphorus rich residue which forms a protective layer on the polymer.¹⁶⁻¹⁹ Therefore the flammability is reduced by the formation of a char by the phosphorus containing materials.²⁰ The higher the char yield, the higher the flame retardancy. In the polycarbonates containing phosphonate groups, the curing was conducted at 350 °C for one hour to ensure the incorporation of phosphonates in polycarbonate.

Wt% of poly cyclic phosphonates	Char yield (%) *	Char yield (%) ^b	Char yield (%) ^c
0	18	18	18
5	45	27	28
10	48	28	40
15	50	28	44

Table 4.1.	Char v	vields of	BPA	pol	ycarbonates	containin	g po	lyphos	phonates

a. BPA polycarbonates containing polycyclic phenylphosphonate resins were cured at 350 °C for 1 hour and heated to 600 °C under oxygen.

b. BPA polycarbonates containing polycyclic phenylphosphonate resins were heated to 600 °C under oxygen.

c. BPA polycarbonates containing polycyclic methylphosphonates were cured at 350 °C for 1 hour and then heated to 600 °C under oxygen.

Polycarbonates with different amounts of phosphonates were then heated to 600 °C under oxygen to obtain the char yield. The char yield of the commercial polycarbonate was 18%. When the polycarbonate was cured in the presence of 5% of a polycyclic phenylphosphonate, the char yield jumped to 45% and it increased up to 50% with 15% of the phosphonates. The char yield data for these materials are presented in Table 4.1. When the uncured mixtures with polycarbonate at different concentrations of polycyclic phenylphosphonates were subjected to similar study, the char yield values were considerably less. This implies that the polycarbonate when cross-linked with the phosphonates should be more flame retardant than the non cross-linked material. Studies were also conducted for polycarbonates containing various amounts of polycyclic methyl phosphonates of 4-t-butylphenol-formaldehyde resins. In this case with 5% polycyclic methyl phosphonate added to polycarbonate, the char yield only went up to 28%. The char yields increased with the increase in phosphonate content.

4.9. Conclusions

Some novel polycyclic phosphonate resins were synthesized by reacting phosphonic dichlorides with p-substituted phenol-formaldehyde resins under high dilution conditions. A secondary amine was used at a later stage in the reaction to react with unreacted -P-Cl groups to convert them to -P-N linkages. MALDI-TOF mass spectrometry was used to detect the absolute masses of these species. The incorporation of phosphorus in these systems was also confirmed by ³¹P NMR. The phosphonates were incorporated into polycarbonates by ring-opening and transesterification reactions with the polycyclic phosphonates. The final thermosetting resins had significantly higher char yields in air compared to commercial BPA polycarbonate alone and BPA polycarbonates with uncured polycyclic phosphonates added.

4.10. Experimental section

Materials

Methylphosphonic dichloride (Aldrich; 98%), phenylphosphonic dichloride (Aldrich; 90%), 4-phenylphenol (Aldrich; 97%), amberlyst-15 (BDH), chlorobenzene (ACP) and formaldehyde (BDH; 36.5-38%) were used as received. 4-t-Butylphenol (Aldrich; 99%) was purified before use. Pyridine (Caledon; 99%) and tetrahydrofuran (Aldrich; 99+%) were distilled before use. Commercial BPA polycarbonate polymer was provided by the General Electric Co.

Characterization techniques

All the mass analyses were performed on a Kratos Kompact MALDI-III mass spectrometer in the reflectron mode. Dithranol and lithium bromide were used as matrix and cationization agent, respectively. All samples were prepared in chloroform. The ratio of polymer to matrix to cationization agent was varied from 1:2:1 to 1:4:1. NMR spectra were taken using a Varian Unity 500 instrument. Seiko 220 DSC and 220 TG/DTA instruments were used to perform thermal studies of the polycyclic phosphonate resins. A heating rate of 20 °C/min was used in both cases. Percent char yields were obtained with a TG/DTA instrument by heating the resins up to 600 °C under oxygen. The heating rate was 20 °C/min.

Gradient HPLC analyses were carried out using a Milton Roy CM 4000 pump equipped with a reverse phase column (prime sphere 5 μ C8, 250x4.6 mm) and a uv detector at 254 nm. The gradient program was as follows: step 1, 70-85% THF over 20 min.; step 2, 85-100% THF over 5 min.; step 3, 100-70% THF over 5 min.; (recycle). The mobile phase was a mixture of THF and water.

General procedure for the synthesis of p-substituted phenol-formaldehyde resins

A 250 mL 3-neck round-bottom flask equipped with a reflux condensor and a nitrogen inlet system was charged with 4-tert-butylphenol (40 g, 0.27 mol), Amberlyst-15 (16 g, 40 wt%), formalin (12 mL, 0.16 mol) and chlorobenzene (40 mL). The reaction mixture was continuously stirred at 100 $^{\circ}$ C for 4 h under nitrogen atmosphere. At the end of the reaction, resin was filtered off and chlorobenzene was rotavapped to give whitish phenol-formaldehyde oligomer powder in 90 % yield.

General procedure for the synthesis of polycyclic phosphonate resins

A 100 mL 3-neck round-bottom flask equipped with a reflux condensor and a nitrogen inlet system was charged with a mixture of 4-phenylphenol-formaldehyde resin (1 g), pyridine (0.7 mL, excess) and THF (46 mL). Phenylphosphonic dichloride (0.6 mL, excess) in THF (8 mL) was added slowly to the reaction mixture over 2 h at 60 °C. The reaction mixture was stirred at this temperature for another 2 h. An aliquot was removed at this juncture and analysed by MALDI-TOF MS which showed the presence of P-Cl linkages in the mixture. The temperature of the reaction flask was lowered to 50 °C and diethylamine (0.5 mL, excess) was added to the mixture which was then stirred for another 4 h. The

final concentration of the resin was 0.1M. The white precipitate of pyridine.HCl was filtered from THF and the filtrate rotavapped to dryness. The solid residue was dissolved in chloroform. This was washed once with 10% aqueous HCl solution and three times with water or until the organic layer became colorless. The organic layer was separated and removed in a rotary evaporator to give the polycyclic phosphonate resin in a 50-55% yield.

Polycyclic phosphonate resin samples for curing study

Polycyclic phosphonates were mixed with a linear polycarbonate in different proportions in methylene chloride. Lithium stearate, 1 mol%, based on the weight of the linear polycarbonate was then added to the mixture. The solvent was evaporated on a hot plate and the sample was then vacuum dried at around 80 °C before curing. Curing studies were conducted in the TG/DTA instrument under nitrogen atmosphere.

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Chapter 5. Polycyclic Siloxanes: Thermally Cross-linkable Intermediates for Polysiloxane Resins

5.1. Introduction

Polyorganosiloxanes have been studied very extensively and they are of great commercial importance.¹⁻³ This is attributed to their extremely low glass transition temperatures which make them useful over a wide temperature range, as well as biocompatibility, high gas permeabilities, atomic oxygen resistance⁴⁻⁶ and a host of other useful properties. One noticeable drawback associated with the polyorganosiloxanes, is their poor mechanical strength. To achieve sufficient mechanical strength they are generally mixed with reinforcing fillers.^{1.2} The polymer-filler interactions are complex phenomena which have to be controlled properly to obtain good properties in the final silicone network. One way of overcoming the processing problem while maintaining good mechanical properties at the same time, is to synthesize block or graft co-polymers by chemically linking soft polysiloxanes with hard segments such as poly(arylene ether sulfones),⁷ polycarbonates,⁸ polyimides⁹ etc. An excellent review on this subject has been provided by Noshay and McGrath.¹⁰

Another approach is to make materials that are easy to process and cross-link them at a later stage to maintain the unique properties of siloxanes with good mechanical strength. Cross-linking in the siloxanes to form networks is done primarily by condensation reactions ¹¹⁻¹² and by free-radical curing.¹³⁻¹⁴ Condensation cure systems are used to give room temperature vulcanized (RTV) silicone rubber. Both high and room temperature vulcanized silicone networks can be formed by free-radical cure mechanisms.

Novolac type phenolic-resins are commonly cured by using 10-15 weight % hexamethylenetetramine. If the cross-link density of the resin is increased substantially to

obtain higher use temperatures or tensile strength for certain applications, they generally become very brittle. If the -Si-O linkage were incorporated in the phenol-formaldehyde resin, it might impart more flexibility to the resin without sacrificing other useful properties. In the present work, the siloxane linkages are incorporated in the phenolic-resin by the functionalization of the hydroxy groups. This is advantageous in the sense that there is no immiscibility or phase separation between the siloxane and the phenol-formaldehyde resin in the uncured state. Ring-opening polymerization (ROP) is used for the synthesis of high molecular weight siloxane polymers. Cyclic trimers or tetramers are subjected to ROP by acid or base catalysts to synthesize high molecular weight siloxane polymers at elevated temperatures.¹⁵⁻¹⁷ The multifunctional polycyclic siloxanes prepared from novolac resins would be expected to undergo a series of ROP reactions along with some polycondensation reactions of unreacted SiOH groups in the presence of a catalyst to give a new type of thermosetting resin with interesting properties.

We have previously characterized p-substituted phenol-formaldehyde resins¹⁸ in chapter 2 by using matrix assisted laser desorption ionization-mass spectrometry (MALDI-MS). MALDI-MS has also been very useful in the present study in the characterization of the absolute masses of the polycyclic siloxanes of phenol-formaldehyde resins.

5.2. Strategy and goals

Our objective in this chapter is to demonstrate the synthesis of polycyclic siloxane derivatives of novolac type resins and cure them at elevated temperatures with a catalytic amount of potassium hydroxide to obtain thermosetting materials. In order to explore the degree of cross-linking, the silicone functionalized phenol-formaldehyde resins were mixed in different proportions with two different types of organo-siloxane gums and their thermal properties studied. The substituents on the silicon atom were altered to produce a few series of polycyclic siloxanes of phenol-formaldehyde resins. The uncured resins were characterized by ¹H and ²⁹Si NMR to confirm the incorporation of siloxane linkages.

5.3. p-substituted phenol-formaldehyde resin

4-t-Butylphenol-formaldehyde resin, which was used as starting resin in the synthesis of polycyclic siloxane resin, was prepared by following the procedure described by us previously ¹⁸ in chapter 2. A MALDI-TOF chart and an HPLC chart of this material are shown in Figure 2.5 and Figure 2.6, respectively. Both charts confirm that there is no high molecular weight material formed in the starting phenolic resin.

5.4. MALDI-TOF MS characterization of polycyclic siloxanes of

4-t-butylphenol-formaldehyde resin

The MALDI-TOF spectrum of the polycyclic dimethylsiloxanes of 4-t-butylphenolformaldehyde is presented in Figure 5.1.



Figure 5.1. MALDI-TOF chart of polycyclic dimethylsiloxanes of 4-t-butylphenolformaldehyde resin

Oligomeric species containing up to three siloxane rings are observed in the MALDI-TOF spectrum. The mass at m/z 477 Dalton (Da) is due to 2-sila-1, 3-dioxane derivative of 4-t-

butylphenol-formaldehyde dimer with a silver ion attached to it (structure A, Scheme 5.1). The mass at 639 Da corresponds to a trimeric monocyclic siloxane with one free phenolic moiety (structure B, Scheme 5.1). The mass at around 800 Da is due to a tetrameric species containing one cyclic siloxane and two free phenolic groups that did not react with the chlorosilane (structure C, Scheme 5.1). The mass at m/z=857 Da is due to a species containing two siloxane rings and one silver ion attached (structure D, Scheme 5.1). The smaller peaks in between masses 857 Da and 1238 Da result from species containing cyclic siloxanes along with free phenolic groups (structures E & F, Scheme 5.1). Usage of Ag⁺ as cationization agent in this case was found to produce better mass spectra.



Figure 5.2. MALDI-TOF chart of polycyclic diphenylsiloxane of 4-t-butylphenolformaldehyde resin

It is quite clear from this data that species containing siloxane rings are much higher in abundance than their counterparts with free phenolic moieties. In addition, there was no signal observed in the MALDI-TOF spectrum corresponding to a species formed by intermolecular reactions of the residual phenolic groups to give linear Si-O-Si linkages.

Figure 5.2 is the MALDI-TOF spectrum of the polycyclic diphenylsiloxanes of 4-tbutylphenol-formaldehyde resin. In this case the most intense signal observed is at m/z=1106 Da which corresponds to a tetrameric bicyclic siloxane species with a silver ion attached to it (structure A, Scheme 5.2). The peak at m/z=1269 Da is most probably due to a pentameric species with two siloxane rings and a free phenolic moiety (structure B, Scheme 5.2).



Scheme 5.1. Proposed structures of polycyclic siloxanes of 4-t-butylphenolformaldehyde resin

The signal at m/z=1467 Da again corresponds to a pentameric species with two siloxane rings in which the free phenolic group reacts with diphenyldichlorosilane to yield $-OPh_2Si-$ Cl which upon workup gets hydrolysed to give $-OPh_2SiOH$ containing species (structure C, Scheme 5.2). The number of siloxane rings observed in this spectrum goes up to 5 which appears as a small peak at the highest mass 2623 Da. The species corresponding to other important signals are presented in Scheme 5.2. The abundance of the species containing free phenolic groups and the ones with $-Ph_2SiOH$ moieties are again significantly lower than the species which only have siloxane rings.



Scheme 5.2. Proposed structures of polycyclic diphenylsiloxane of 4-t-butylphenol-

formaldehyde resin

5.5. HPLC characterization of polycyclic diphenylsiloxane

A gradient HPLC chart of this material is presented in Figure 5.3. The intensities of cyclic siloxane species in both MALDI-TOF and in HPLC match quite well. This again confirms the presence of significantly higher amount of cyclic siloxane species. Furthermore, the HPLC chart does not show the presence of any high molecular weight polymer.



Figure 5.3. Gradient HPLC chart of polycyclic diphenylsiloxane of 4-t-butylphenolformaldehyde resin

5.6. MALDI-TOF MS characterization of polycyclic siloxanes of 4-phenylphenol-formaldehyde resin

The MALDI-TOF chart of the 4-phenylphenol-formaldehyde resin prior to functionalization with diphenyldichlorosilane is presented in chapter 3 (Figure 3.5). The oligomeric phenol-formaldehyde resin contains up to 14 repeat units. The MALDI-TOF spectrum of the polycyclic diphenylsiloxanes of 4-phenylphenol-formaldehyde resin is presented in Figure 5.4. The mass at m/z=640 Da (structure A, Scheme 5.3) refers to a monocyclic siloxane with a attached silver ion. The mass at m/z=822 Da (structure B, Scheme 5.3) is due to a trimer with one siloxane ring and a free phenolic group. The mass at m/z=838, however, is most likely due to a species with two free phenolic groups and the third one being replaced by a $-Ph_2SiOH$ group (structure C, Scheme 5.3). Similarly, the mass at m/z=1004 Da refers to a tetrameric species with two free phenolic groups (structure

D, Scheme 5.3), whereas the other small peak in this doublet at m/z=1019 Da is most probably due to a species with three free phenolic moieties and the fourth one being substituted by a -Ph₂SiOH group (structure E, Scheme 5.3). The presence of these types of species is likely the outcome of the comparatively low reactivity of diphenyldichlorosilanes with 4-phenylphenol-formaldehyde resins. The intensities of these signals are smaller, corresponding to the lower abundance of these oligomers. The most intense signal in this series is due to a bicyclic siloxane resin (structure F, Scheme 5.3). The other intense signal at m/z=1367 Da represents a pentameric species with two siloxane rings and a free phenolic group (structure G, scheme 5.3).



Figure 5.4. MALDI-TOF chart of polycyclic diphenylsiloxane of 4-phenylphenolformaldehyde resin

The number of siloxane rings observed in these systems gradually increases while the signal intensities go down accordingly indicating the lower abundance of the higher

oligomers. The oligomeric species comprising tetracyclic siloxane rings at mass 2276 Da is still clearly visible in the MALDI-TOF spectrum. The presence of species containing free Si-OH moieties would presumably not be a problem in the final cross-linking reaction since the free silanol groups would most likely form Si-O-Si linkages via polycondensation reactions.



Scheme 5.3. Proposed structures of polycyclic diphenylsiloxanes of 4-phenylphenolformaldehyde resin

5.7. Characterization by NMR

Both ¹H and ²⁹Si NMR have been very useful in the characterization of the polycyclic siloxanes. A portion of the ¹H NMR spectrum of the polycyclic dimethylsiloxanes of 4-t-butylphenol-formaldehyde resins is shown in Figure 5.5. Methyl protons attached to siloxane linkages appear as a multiplet at around 0.0 ppm due to the different electronic environments experienced by these protons. The tertiary butyl protons for an eight

membered siloxane ring of a phenol-formaldehyde dimer is 3 to 1. The ratio observed in the ¹H NMR spectrum is 2.9. This implies that most of the starting 4-t-butylphenolformaldehyde resin formed cyclic siloxane species. The methylene bridged protons appear as a multiplet at around 3.85 ppm and very low intensity signals for the free phenolic group show up between 4.8 and 5.6 ppm.



Figure 5.5. ¹H NMR spectrum of polycyclic dimethylsiloxane of 4-t-butylphenolformaldehyde resin

Figure 5.6 is a similar ¹H NMR spectrum of the polycyclic diphenylsiloxanes of 4-tbutylphenol-formaldehyde resin. The tertiary butyl protons again appear as a multiplet at around 1.25 ppm. The methylene bridged protons in this case, however, appear in the range between 3.4 and 4.4 ppm. This is most likely because the methylene groups inside the siloxane rings experience different electronic and steric environment as a result of the bulky phenyl groups on silicon. A few peaks of lower intensities again appear between 4.8 and 5.6 ppm due to the presence of species with free phenolic groups. The phenyl protons attached to siloxane appear between 6.0 and 8.0 ppm. The ²⁹Si NMR spectrum of the polycyclic diphenylsiloxanes of 4-phenylphenol-formaldehyde resin is presented in Figure 5.7. The appearance of a few peaks between -32 and -44 ppm is an indication of the incorporation of diphenylsiloxane linkages into the novolac type resin. In addition, there are at least eight different silicons with different electronic environments which again demonstrates the presence of multiple oligomeric polycyclic siloxane species.



Figure 5.6. ¹H NMR spectrum of polycyclic diphenylsiloxane of 4-t-butylphenolformaldehyde resin



Figure 5.7. ²⁹Si NMR spectrum of polycyclic diphenylsiloxane of 4-phenylphenolformaldehyde resin

5.8. Cross-linking study

Some preliminary curing studies were conducted in order to assess whether the cross-linking reactions would occur in these polycyclic siloxanes to eventually obtain thermosetting materials. A neat sample of polycyclic diphenyl siloxane of 4-phenylphenol-formaldehyde resin was cured at different temperatures for varying lengths of time in order to establish the optimum curing condition. In addition, the stability of the polycyclic resin was evaluated at the curing temperature. The thermal properties of the polycyclic resin are presented in Table 5.1. The T_g of the polycyclic diphenyl siloxane resin was 113 °C. When the polycyclic resin was cured at 300 °C for 30 min in the presence of 1 mol% KOH, no T_g was observed, indicating a high degree of cross-linking in the system under these curing conditions. Also, a 4% weight loss was observed after the resin was cured at 300 °C for 30 min. This shows that the polycyclic resin in the presence of KOH is sufficiently stable under the curing conditions.

Curing temp. (°C)	Curing time (min)	Tg (°C)	% Wt. loss	
N/A	N/A	113	N/A	
250	15	136	0	
300	15	156	4	
300	30	none	4	

 Table 5.1. Thermal profile of polycyclic diphenylsiloxane of 4-phenylphenolformaldehyde resin

Two series of materials were prepared by using two different commercial siloxane polymers mixed with two types of polycyclic siloxanes in different proportions. Each sample was cured at 300 "C for 30 minutes. The T_g of commercial polydimethylsiloxane gum is -128 °C. When this material was cured with up to 20 wt % polycyclic

dimethylsiloxane resin, no change in glass transition temperature was observed. With 30 wt % polycyclic siloxane added no T_g was observed. In each case, however, a cross-linked insoluble material was obtained after the curing. This implies that in each case a few cross-links were formed but they were presumably not high enough to restrict the segmental motions of the polymeric chains. Hence no impact on T_g was evident. Chloroform was used as a solvent to test the solubility of the cross-linked material. The curing data is presented in Table 5.2.

 Table 5.2. Curing data of a polydimethylsiloxane gum with different polycyclic siloxane resin content

% polycycli siloxane resin	c T _g (°C)	Curing temp. (°C)	Curing time (min.)
0	-128	none	none
10	-128	300	30
20	-128	300	30
30	none	300	30

Similar results were obtained when poly(dimethylsiloxane-*co*-diphenylsiloxane) gum was cured with different wt % of the polycyclic diphenylsiloxane resins. It has been documented that a silicone gum depolymerizes and loses over 99% of its weight when kept at 250 °C for 20 h in the presence of a trace amount of KOH.¹⁹ A 60% weight loss was observed when a poly(dimethylsiloxane-*co*-diphenylsiloxane) gum was cured at 300 °C for

30 min in the presence of 1 mol% of KOH. Since the gum constitutes 90% dimethyl siloxane units, it could very possibly form some cyclics such as D_3 , D_4 , etc. and some linear oligomers. A substantial weight loss at 300 °C is indicative of the evaporation of lower cyclics and linear oligomers from the gum sample. When 10 wt % of polycyclic diphenyl siloxane resin was incorporated into the silicone gum and cured under the same conditions, the weight loss was reduced to 33%. The % weight loss values showed a decreasing trend with the incorporation of higher amounts of polycyclic resin in the gum sample. At 30 wt % loading of the polycyclic resin, the weight loss was significantly reduced to a value of 7%. This implies that as the concentration of polycyclic siloxane resin in the gum. At a 30 wt % concentration of the polycyclic resin, presumably the cross-linking would predominate resulting in a low % weight loss value.



Figure 5.8. DSC scans of cured and uncured siloxane gum

Unreacted Si-OH bonds are known to undergo polycondensation reactions to form Si-O-Si linkages.²⁰ Therefore, cross-linking by condensation reactions of the species containing free Si-OH groups is feasible. However, in all the polycyclic resins studied, the species containing complete polycycles show much higher abundance in the MALDI-TOF MS as well as in the gradient HPLC spectra. Therefore, most probably, cross-linking by ring-opening polymerization is the favored route. Nevertheless, formation of Si-O-Si linkages by condensation of the silanol groups can not be ruled out. The final cross-linked materials therefore would be formed presumably by a combination of ROP of the cyclic siloxanes and condensation reactions of the residual Si-OH groups. A typical DSC scan of the uncured and cured material is presented in Figure 5.8. No T_g was observed when the commercial gum was cured with polycyclic diphenylsiloxane at and above 30 wt % concentration.

5.9. Conclusions

Polycyclic siloxanes with both dimethyl and diphenyl substituents on silicon were synthesized by reacting dimethyl and diphenyl chlorosilanes with para-substituted novolac resins under high dilution conditions. MALDI-TOF MS was used extensively in the characterization of the absolute masses of the different species formed in the product mixture. Both ¹H and ²⁹Si NMR were very useful as complementary techniques in the structural characterization of the polycyclic siloxane resins. Optimum temperature for curing the polycyclic siloxane resin and the blend of silcone gum and polycyclic siloxanes was found to be 300 °C. A high concentration of polycyclic siloxane was needed in the silicone gum mixtures in order to obtain a highly cross-linked network.

5.10. Experimental section Materials

Diphenyldichlorosilane (United Chemical Technology), amberlyst-15 (BDH), chlorobenzene (ACP), formaldehyde (BDH; 36.5-38%), 4-phenylphenol (Aldrich; 97%) and polydimethylsiloxane gum (United Chemical Technology) were used as supplied. 4-t-Butylphenol (Aldrich; 99%) was recrystallized from hexanes prior to use. Dichlorodimethylsilane (Aldrich; 99%), pyridine (Caledon; 99%) and tetrahydrofuran (Aldrich; 99+%) were distilled before use. Polydimethyl (90%) polydiphenyl (10%) siloxane co-polymer gum was kindly provided by General Electric Silicones.

Characterization techniques

A Kratos Kompact MALDI-III mass spectrometer was used for the mass analysis in the reflectron mode. Dithranol and silver trifluoroacetate were used as matrix and cationization agent, respectively. Dithranol was dissolved in chloroform whereas THF was used to prepare silver trifluoroacetate. The samples were prepared in chloroform. The ratio of polymer to matrix to cationization agent was 1:2:1.

A Milton Roy CM 4000 pump equipped with a reverse phase column (prime sphere $5 \mu C8$, 250X4.6 mm) and a uv detector at 254 nm was used to carry out gradient HPLC analyses. The eluent was a mixture of THF and water. The gradient program was as follows: step 1, 75-95% THF over 20 min.; step 2, 95-100% THF over 5 min.; step 3, 100-75% THF over 5 min.; (recycle). NMR spectra were recorded using a Varian Unity 500 instrument. In the case of ²⁹Si NMR measurements chromium-III-acetylacetonate was added to the sample solutions to reduce the T₁-relaxation time. A Seiko 220 TG/DTA instrument was used to perform the curing study of polycyclic siloxane resins. This was done under nitrogen atmosphere with a flow rate of 200 mL/min and a heating rate of 20 °C/min. The T_g s of the polycyclic siloxane resins were determined with a Seiko 220 DSC. A Perkin-Elmer DSC 7 was used to study the glass transition temperatures of the uncured and cured silicone gums with different proportions of polycyclic siloxanes under
nitrogen. The samples were cooled to -140 °C and a heating rate of 10 °C/min was applied. Inherent viscosities of the two commercial silicone gums in chloroform were measured using an Ubbelohde viscometer thermostatted at 25 °C.

General procedure for the synthesis of polycyclic dimethylsiloxane resins A 250 mL 3-neck round-bottom flask equipped with a reflux condensor and a nitrogen inlet system was charged with a mixture of 4-t-butylphenol-formaldehyde resin¹⁸ (8 g), pyridine (10.0 mL, excess) and THF (100 mL). Dichlorodimethylsilane (8.0 mL, excess) in THF (60 mL) was added slowly to the reaction mixture over 3 h at 30 °C. The reaction mixture was stirred at 30 °C for another 2 h. The white precipitate of pyridine.HCl was filtered from the THF solution and the filtrate rotary evaporated to dryness. The residue was dissolved in chloroform and then washed once with 10% HCl and three times with water. The organic layer was seperated and removed in a rotary evaporator to give an oily product. The isolated yield of the product was 70-75%.

General procedure for the synthesis of polycyclic diphenylsiloxane resins A mixture of 4-phenylphenol-formaldehyde resin¹⁸ (1 g), pyridine (0.5 mL, excess) and THF (46 mL) was charged into a 100 mL 3-neck round-bottom flask equipped with a reflux condensor and a nitrogen inlet system. Dichlorodiphenylsilane (0.6 mL) in THF (8 mL) was added to the reaction mixture over a period of 2 h under nitrogen atmosphere. The temperature of the reaction flask was maintained at around 50 °C. The reaction mixture was stirred for another 4 h after the addition was complete. The white precipitate of pyridine.HCl was filtered from the THF solution and the mixture rotavapped. The residue was dissolved in a minimum amount of chloroform and this was precipitated in 200 mL of methanol. A white solid product was obtained. The product yield in this case was about 30%.

Preparation of polycyclic siloxane resins for curing study

Two different types of polysiloxane gums were chosen for the cross-linking study. Polycyclic dimethylsiloxane resin was mixed with polydimethylsiloxane gum ($\eta_{inh} = 1.34$ dL/g) whereas polycyclic diphenylsiloxane resin was mixed with poly(dimethylsiloxaneco-diphenyl siloxane) gum (η_{inh} =1.29 dL/g) to achieve better miscibility of the chains. The samples were dissolved in methylene chloride solution and 1 mol% powdered KOH was added (based on the weight of the gum). The solutions were evaporated on a hot plate and vacuum dried in an oven at 80 °C before curing. Neat samples of polycyclic diphenyl siloxane resin and poly(dimethyl siloxane-co-diphenyl siloxane) gum were also prepared by using the above method in order to carry out parallel curing studies. The curing studies were performed in TG/DTA instrument at different temperatures under nitrogen atmosphere.

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Chapter 6. Synthesis and Characterization of some Novel Polycyclics and Co-polymers from a Bisphenol A Dimer

6.1. Introduction

In recent years, synthesis of macrocyclic oligomers as precursors to high performance thermoplastic materials has been studied extensively because of the ease of processability of the mixed cyclics which is attributed to their low melt viscosities.¹⁻⁸ After fabrication the mixed cyclics can be converted to high molecular weight polymers⁹⁻¹¹ by ring-opening polymerization (ROP). Macrocyclic poly(aryl ether)s ¹²⁻¹⁸ and sulfides ¹⁹⁻²¹ have been synthesized and the ring-opening polymerization of these cyclics studied. Synthesis of single-sized macrocycles has also been investigated in order to better understand and control the ROP process.^{22,23} In all these cases, the cyclics have been prepared from bifunctional monomers. The synthesis of cyclics from a tetrafunctional starting material would be expected to be comparatively more challenging because of the difficulty in avoiding cross-linking reactions.

In an effort to synthesize oligomeric polycyclics as precursors to thermosetting materials, we started with a tetrafunctional o, o'-methylene bridged Bisphenol A dimer. A similar dimer has been synthesized earlier by a six-step protection-deprotection sequence. ²⁴ The tetrafunctional dimer, in the present study, was conveniently synthesized by a single-step, one-pot reaction.

Polymers containing reactive functionalities have been synthesized in the past in order to obtain thermosetting polymer matrices by cross-linking reactions of the reactive sites, thermally or photochemically. ²⁵⁻²⁸

6.2. Strategy and goals

Our objective, in this chapter, is to report a convenient one-step synthesis of a tetrafunctional BPA dimer and the synthesis of a series of novel oligomeric polycyclic structures from the dimer, as precursors to thermosetting resins. Our efforts have also been directed toward the synthesis of BPA co-polycarbonates with internal cross-linkable moieties by incorporating different proportions of BPA dimer into BPA and conversion of the mixture to a polycarbonate.

6.3. Synthesis and characterization of o, o' methylene

bridged BisphenolA dimer 2

The synthetic route for the preparation of dimer 2 is presented in Scheme 6.1. Because of the availability of four reactive sites ortho to the phenolic hydroxyl groups, a large excess of BPA (15 equivalent) was needed to avoid formation of any higher oligomers and to obtain dimer 2 as a single product. The present method of synthesizing the dimer is attractive because it is a simple, one-pot reaction with a reusable catalyst. No extensive work-up was necessary. The excess starting material could be easily removed by distilling under reduced pressure and recycled.



Scheme 6.1 Route to the synthesis of Bisphenol A dimer 2

The MALDI-TOF spectrum of the dimer is presented in Figure 6.1. 15 equivalents of BPA for each equivalent of formaldehyde was found to be the optimum concentration to obtain pure dimer. Appearance of a singlet at 3.7 ppm in the ¹H NMR is a confirmation of the o, o' methylene bridged protons. In addition, the integration values of different protons of the dimer gave an excellent match. The purity of the dimer is further reflected in the ¹³C NMR spectrum. Only thirteen different carbon signals were obtained that are representative of different carbons of the dimer. The presence of a signal at 30 ppm is another evidence of the presence of o, o' methylene bridge carbon. ²⁴



Figure 6.1 MALDI-TOF spectrum of BPA dimer 2

6.4. Synthesis and characterization of oligometric polycyclic phosphonates

We have reported the synthesis and cross-linking study of the polycyclic phosphonates of p-substituted phenol-formaldehyde resins in chapter 4.²⁹ These cross-linked resins exhibited good flame-retardant properties. In order to extend our previous study, we report in a part of this chapter a facile synthesis of oligomeric polycyclic

phosphonates by reacting the tetrafunctional BPA dimer 2 with phosphonic dichlorides under high dilution conditions. The synthetic method is presented in Scheme 6.2. Both the methyl and phenyl phosphonic dichlorides reacted readily with the dimer under high dilution conditions, to generate soluble predominantly polycyclic, oligomers. The MALDI-TOF chart of the oligomeric polycyclic phenyl phosphonates is shown in Figure 6.2. The number of repeat units (n) ranges from 1 to 3.



Scheme 6.2 Synthetic route to oligomeric polycyclic phosphonates



Figure 6.2 MALDI-TOF spectrum of oligomeric polycyclic phenylphosphonates

The signal observed at m/z=2144 Dalton (n=3 +Li) represents a tetracyclic phenylphosphonate with three 8-membered rings and one 60-membered ring. In addition to the predominant presence of complete polycyclics there were also some signals in the mass spectrum corresponding to partly cyclic short chain linear oligomers. For example, the signal at m/z=880 Da, most likely represents a monocyclic phosphonate and a lithium ion with acidic end-groups as shown by the structure on the chart. The gradient HPLC of the phosphonate polycyclics is shown in Figure 6.3.



Figure 6.3 Gradient HPLC chart of oligomeric polycyclic phenylphosphonates

The HPLC chart showed the presence of polycyclic species. The smaller signals in between the complete polycyclic species are most likely due to the partly cyclic phosphonate species with acidic end-groups. Because of the similar polarity of the species containing acidic end-groups, the peaks have similar retention times. It also confirmed that no linear polymer of high molecular weight was formed in the reaction. The ¹H NMR

spectrum of the oligomeric polycyclic phenylphosphonates in $CDCl_3$ is shown in Figure 6.4.



Figure 6.4 ¹H NMR of oligomeric polycyclic phenylphosphonates



Figure 6.5 MALDI-TOF MS of oligomeric polycyclic methylphosphonates

The isopropylidene protons center around 1.4 ppm. The o, o' methylene bridged protons appear at around 3.8 ppm and the aromatic protons appear as a complex multiplet in the range of 6.4 to 8.2 ppm. The MALDI-TOF chart of oligomeric polycyclic methylphosphonates is presented in Figure 6.5. This also showed the predominant presence of polycycles with n=1, 2 and 3 in the product mixture.

6.5. Synthesis and characterization of oligomeric polycyclic siloxanes



Figure 6.6 MALDI-TOF of oligomeric polycyclic dimethylsiloxanes

Oligomeric polycyclic siloxanes were synthesized in a similar fashion to that of the polycyclic phosphonates. The MALDI-TOF chart of oligomeric polycyclic dimethylsiloxanes is presented in Figure 6.6. The predominance of polycyclics is quite apparent from the spectrum. In this case the number of repeat units (n) ranges from 2 to 5. The most intense signal at m/z=1167 Da represents a tricyclic siloxane with a lithium ion attached. The smaller signal at m/z=1145 Da is most likely due to the loss of a methyl group from the parent ion (m/z=1160 Da) to give a radical cation. The gradient HPLC

chart of the polycyclic siloxanes is presented in Figure 6.7. It also showed the presence of polycyclic species. In addition, it also showed the presence of small amounts of linear polymer of higher molecular weights. The ¹H NMR spectrum is shown in Figure 6.8. The incorporation of $-(CH_3)_2$ SiO functionality is evident from this spectrum. The methyl protons attached to Si appear at 0.0 ppm.



Figure 6.7 Gradient HPLC of oligomeric polycyclic dimethylsiloxanes



Figure 6.8 ¹H NMR of oligomeric polycyclic dimethylsiloxanes

6.6. Synthesis and characterization of oligomeric polycyclic carbonates

The method of synthesis of oligomeric polycyclic carbonates is somewhat different from those of the aforementioned polycyclics. The optimum conditions were obtained by mixing the dimer and triphosgene together and then adding the mixture slowly to the reaction vessel containing the base, to give high dilution conditions in order to avoid intermolecular reactions. The MALDI-TOF spectrum is shown in Figure 6.9.



Figure 6.9 MALDI-TOF MS of oligomeric polycyclic carbonates

The number of repeat units in the polycyclics went up to n=6. Signals due to some linear oligomers containing in part cyclic moieties were also observed. For example, the signal at m/z=2088 Da represents a pentacyclic species with four 8-membered rings and one 80-membered ring whereas the peak at m/z=2061 Da would most probably be due to a linear species with hydroxy end-groups and four 8-membered rings on the backbone.

6.7. Synthesis and cross-linking study of BPA co-polycarbonates

Synthesis of BPA co-polycarbonates by incorporating the dimer 2 into the structure is presented in Scheme 6.3.



Scheme 6.3 Synthetic route to BPA co-polycarbonates



Figure 6.10 Gel Permeation Chromatograph of BPA co-polycarbonates

BPA co-polymers containing the tetrafunctional dimer in the backbone would be expected to undergo cross-linking upon heating in the presence of a transesterification catalyst. The highest amount of the dimer that could be incorporated before the reaction started gelling was 3.5 mole percent of the dimer for each mole of BPA. The GPC of the polymer shown in Figure 6.10 had $M_w=20,000$ g/mol. Hence a moderately high molecular weight polymer can be obtained before the occurrence of cross-linking.

Our next objective was to co-polymerize a mixture of BPA and BPA dimer prepared *in situ* with triphosgene to obtain co-polycarbonates with the internal cyclic carbonate moieties. This was advantageous in that prior separation and purification of the dimer was not necessary. Since 3.5 mole percent of the dimer gave reasonably high molecular weight polymer, we incorporated the same amount of dimer prepared *in situ* in excess BPA. This required 30 equivalents of BPA for each equivalent of formaldehyde to obtain 3.5 mole percent of the dimer in the product mixture.



Scheme 6.4 Synthetic route for in situ preparation of BPA co-polycarbonates

A comparison of the average molecular weights and GPC patterns with those obtained by physically incorporating the dimer to obtain co-polycarbonates was carried out. The *in situ* polymerization method is shown in Scheme 6.4. Once the dimer 2 was prepared in the usual manner, the solvent THF was removed under reduced pressure. The mixture of BPA and BPA dimer was then dissolved in dichloromethane with the addition of a base and triphosgene was added slowly to the reaction mixture at 30 °C. The slow addition of triphosgene was necessary in order to avoid cross-linking during polymerization reaction. The co-polycarbonate obtained had a similar GPC pattern (Figure 6.11) with M_w around 20,000 g/mol.



Figure 6.11 GPC of BPA co-polycarbonates prepared in situ

The polymers were subjected to curing studies at elevated temperatures in the presence of tetrabutylammonium tetraphenylborate catalyst. This catalyst system has been used previously for the ring-opening polymerization of cyclic oligomeric carbonates. ^{4,5} The thermal profile is presented in Table 6.1. The uncured polymer had a T_g of 130 °C.

When the polymer was cured at 350 °C for 30 minutes, the T_g went up to 180 °C. The cured polymer was completely insoluble in chloroform indicating the formation of a highly cross-linked material.

Curing temp. (°C)	Curing time (min)	T _g (°C)
N/A	N/A	130
300	15	147
350	15	167
350	30	180

Table 6.1 Curing data of BPA co-polycarbonates

6.8. Conclusions

An o, o' methylene bridged BPA dimer 2 has been conveniently synthesized by a one-step process. Three different classes of oligomeric polycyclics have been synthesized from the dimer 2 in relatively high yield by its reaction with corresponding dihalo compounds under high dilution conditions. These polycyclics could potentially be used as precursors to thermosetting resins. BPA co-polycarbonates with internal cross-linking moieties were synthesized by reacting a mixture of BPA and dimer 2 with solid triphosgene. The co-polycarbonates were also synthesized with BPA dimer prepared *in situ* which furnished the same average molecular weights. When the co-polycarbonate was cured at 350 °C for 30 minutes, a 50 °C increase in T_g was observed. The cured material was highly cross-linked.

6.9. Experimental section

Materials

Bisphenol A (Aldrich; 97%), Amberlyst-15 (BDH), formaldehyde (BDH; 36.5-38%), 98%), methylphosphonic dichloride (Aldrich; 98%), triphosgene (Aldrich; dichloride 90%) received. phenylphosphonic (Aldrich: were used as Dichlorodimethylsilane (Aldrich; 99%), pyridine (Caledon; 99%), triethylamine (Aldrich; 99%), tetrahydrofuran (Caledon; 99%) and dichloromethane (Caledon; 99.5%) were distilled before use.

Characterization techniques

A Kratos Kompact MALDI-III mass spectrometer in the reflectron mode was used for mass analysis. Dithranol dissolved in chloroform was used as a matrix in all cases. Lithium bromide or silver trifluoroacetate in tetrahydrofuran were used as cationization agents to obtain good signal to noise ratios. Each mass spectrum represents an average of one hundred laser shots.

GPC analyses were recorded on a Waters 510 HPLC using four phenogel 5 μ m columns (1 linear, 3x500 Å) arranged in series with chloroform as an eluent. The flow rate was 1 mL/min. The uv detector was set at 254 nm and polystyrene was the external calibrant.

Gradient HPLC analyses were performed on a Milton Roy CM 4000 pump equipped with a reverse phase column (prime sphere 5 μ C8, 250X4.6 mm) and a uv detector at 300 nm. The gradient program was as follows: step 1, 70-95% THF over 20 min.; step 2, 95-100% THF over 5 min.; step 3, 100-70% THF over 5 min.; (recycle). A mixture of THF and water was used as a mobile phase.

A Varian Unity 500 instrument was used to record the NMR spectra. A Seiko 220 TG/DTA was used to cure the BPA co-polycarbonates at different temperatures. A Seiko 220 DSC at a heating rate of 20 $^{\circ}$ C/min under nitrogen was used to study the effect of curing on T_g of these polymers.

Synthesis of O, O' methylene bridged BPA dimer (2)

Bisphenol A (20 g, 87.6 mmol), Amberlyst-15 (4 g, 20 wt.%) and tetrahydrofuran (150 mL) were charged into a 300 mL 3-neck round-bottom flask equipped with a reflux condensor and a nitrogen inlet. Formaldehyde (37%, 0.4 mL, 5.3 mmol) was added to the mixture when all the BPA went into the solution. The mixture was continuously stirred at 60 °C for 4 h. At the end of the reaction the ion-exchange resin was filtered off and THF was removed in a rotary evaporator. The solid residue was then dissolved in a minimum amount of ethyl acetate and passed through a bed of silica with hexane:EtOAc (3:7) as eluent, to get rid of any possible acidic impurities . Excess BPA was then distilled off in a kugelrohr distillation apparatus at 170 °C under reduced pressure. The pale yellow solid obtained was recrystallized from chloroform to give a white o, o' methylene bridged BPA dimer. The isolated yield of the dimer was 60%. mp 204-205 °C. ¹³C NMR (500 MHz, DMSO) : δ (ppm) 155.12, 152.90, 141.46, 141.10, 128.46, 127.60, 126.22, 125.15, 114.81, 114.48, 41.15, 31.20, 29.81.

¹H NMR (500 MHz, DMSO) : δ (ppm) 9.07 (s, 40H), 6.75 (m, 14H), 3.68 (s, 2H), 1.44

(s, 12H). FABMS (nitrobenzyl alcohol matrix) $468(M^*)$, $469(M^* + 1)$, $470(M^* + 2)$.

General procedure for the synthesis of oligomeric polycyclic phosphonates

To a 100 mL 3-neck round-bottom flask equipped with a reflux condensor, a nitrogen inlet and a dropping funnel, were added BPA dimer (0.4 g, 0.85 mmol), triethylamine (0.6mL, 4.3 mmol), and THF (24 mL). Methylphosphonic dichloride (0.2 mL, 2.2 mmol) in THF (16 mL) was added dropwise to the reaction mixture over a 3 h period at room temperature. The reaction temperature was raised to 30 $^{\circ}$ C after the addition was complete. The reaction mixture was then stirred for another 4 to 5 h. The final concentration of the product was 20 mM. The white precipitate was filtered off and THF removed in a rotary evaporator under vacuum. The solid residue was dissolved in chloroform and washed a few times with water. The organic layer was then removed under vacuum to afford a mixture of oligomeric polycyclic phosphonates in 94% yield. The mixed polycyclic phenylphosphonates had mp = 205-215 °C. The mp of the oligomeric polycyclic methylphosphonates was 195-205 °C.

General procedure for the synthesis of oligomeric polycyclic siloxanes

A 100 mL 3-neck round-bottom flask fitted with a reflux condensor and a nitrogen inlet system was charged with BPA dimer (0.4 g, 0.85 mmol), triethylamine (0.6 mL, 4.3 mmol) and dichloromethane (24 mL). Dichlorodimethylsilane (0.24 mL, 1.98 mmol) in dichloromethane (16 mL) was added to the reaction flask via a syringe pump over 3 h at 30 $^{\circ}$ C. The reaction mixture was stirred for another 3 h after the addition was complete. The final product concentration was 20 mM. The organic layer was washed with water a few times and then the solvent removed to yield a mixture of oligomeric polycyclic siloxanes in 80 % yield. The mixed polycyclic siloxanes had mp (90-95 $^{\circ}$ C).

Synthesis of oligomeric polycyclic carbonates

A 50-mL 3-neck round-bottom flask equipped with a reflux condensor and a nitrogen inlet system, was charged with triethylamine (0.3 mL, 2.15 mmol) and tetrahydrofuran (12 mL). A mixture of the BPA dimer (0.2 g, 0.43 mmol), triphosgene (0.1 g, 1 mmol) and THF (8 mL) was added to the reaction flask slowly within a period of 3 h at 30 °C via syringe pump. The final concentration of the product was 20 mM. The reaction mixture was stirred for another 3 h after the addition was complete. The white precipitate was filtered off and the solvent was removed under reduced pressure. The solid residue was dissolved in chloroform and washed once with 10% hydrochloric acid and three times with water. The organic layer was then rotary evaporated to obtain an off-white solid in 40% yield.

General procedure for the synthesis of BPA co-polycarbonates

A 25 mL 3-neck round-bottom flask equipped with a reflux condensor and a nitrogen inlet system was charged with BPA (1 g, 4.4 mmol), 2 (0.08 g, 0.2 mmol), pyridine (0.9 mL, 11 mmol) and dichloromethane (4 mL). Triphosgene (0.6 g, 6 mmol) in dichloromethane

(3.7 mL) was added to the reaction flask via a syringe pump over 3 h. The final solids content was 15 weight percent. The reaction mixture was stirred at 30 °C for another 3 h. The precipitate was filtered off and the filtrate was washed once with 10% hydrochloric acid and three times with water. The dichloromethane solution was poured into methanol and the white polymer was collected by filtration. The polymer was dissolved in chloroform and reverse precipitated from methanol to remove low molecular weight oligomers.

General procedure for in-situ polymerization of BPA co-polycarbonates

To a 100 mL 3-neck round-bottom flask fitted with a reflux condensor and a nitrogen inlet was added BPA (2 g, 8.8 mmol), cation-exchange resin (0.4 g, 20% by weight) and THF (15 mL). The flask was then placed in a pre-heated oil bath maintained at 70 °C and (37%) formaldehyde (0.022 mL, 0.29 mmol) was then added to the reaction mixture. The mixture was stirred at this temperature for 4 h and the cation-exchange resin was then filtered off and THF was removed under reduced pressure. The solid residue was mixed with dichloromethane (6 mL) and transferred to a 50 mL 3-neck round-bottom flask fitted with a reflux condensor and a nitrogen inlet system. Triethylamine (2.6 mL, excess) was added to the reaction flask to dissolve the reactants. Triphosgene (1 g. excess) in dichloromethane (5 mL) was added to the reaction flask via syringe pump in 2-3 h at 30 $^{\circ}$ C reaction temperature. The solids content was kept at 15 wt %. The reaction mixture was stirred for another 2 h after the addition of triphosgene was complete. The white precipitate was filtered off and after the usual work-up as described in the previous section, the dichloromethane solution was added to methanol. Due to the presence of some low molecular weight oligomers, the polymer was dissolved in chloroform and reverse precipitated from methanol.

Preparation of polymer samples for curing studies

BPA co-polycarbonate polymer was dissolved in dichloromethane solution. Tetrabutylammonium tetraphenyl borate, 1 mol%, based on the weight of the polymer was then added to the solution. Dichloromethane was removed and the polymer sample was vacuum dried at 80 °C before curing.

6.10. References and notes

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Chapter 7. Synthesis of Poly(ether sulfone)s End-capped with Metal containing Phthalocyanines

7.1. Introduction

Phthalocyanines are used as dyestuffs in inks and also in the clothing industry.¹ In recent years there has been an upsurge in research activities centered around phthalocyanine chemistry because of the recognition of its many interesting properties which find applications in the polymer and materials science arenas. To name a few, they are applied as photoconductors in xerography,² as non-linear optical materials, ³⁻⁶ and also in liquid crystal displays⁷ and molecular electronic devices.¹ Another important use of phthalocyanines is their applicability as sensitizers in photodynamic cancer therapy.⁸

In the early 1930s Linstead and co-workers reported the synthesis of various phthalocyanines.⁹⁻¹² One of the inherent processing problems associated with phthalocyanines is their insolubility in organic solvents.^{1,13} Improvements in solubility have been made by attaching flexible organic groups to phthalocyanines.¹ Incorporating the phthalocyanines into polymers also improves their solubility. Phthalocyanines have been incorporated into the polymer backbone in a variety of ways. Sometimes the ligand or the central metal atom forms part of the polymer chain. The metal phthalocyanines have also been bound to the polymer chain by covalent bonds or the central metals are sometimes co-ordinatively bound to a donor ligand on the polymer chain.¹ Synthesis of covalently bound phthalocyanines or its analogs to the polymer chain has previously been reported by our group.¹⁴

7.2. Strategy and goals

As a continuation of our efforts to improve processability, our objective, in this chapter, is to demonstrate the synthesis of thermally stable polymers end-capped with metal-phthalocyanine rings.

Synthesis of phthalonitrile end-capped polymers as thermosetting resins has been described by Keller.¹⁵⁻¹⁷ In a similar fashion we synthesized o-phthalonitrile end-capped poly(aryl ether sulfone)s by reacting the corresponding oligomeric bisphenoxy salts with 4-nitrophthalonitrile. The o-phthalonitrile end-capped poly(aryl ether sulfone)s were then reacted with excess phthalonitrile in the presence of a metal or metal salt in a high boiling solvent to obtain phthalocyanine end-capped poly(aryl ether sulfone)s.

It has been reported that the electronic conductivitiy of phthalocyanines arises from their tendency to stack in the solid state.¹⁸ We have prepared a series of relatively low molecular weight PcM (M=Cu, Fe) end-capped poly (aryl ether sulfone)s and the aggregation phenomenon of the PcM rings was studied. A potential advantage of endcapping poly(aryl ether sulfone)s with PcM moieties is that the properties of high molecular weight polymers could possibly be obtained from the corresponding low molecular weight polymers, presumably because of the stacking of the phthalocyanine rings in the solid state. In the melt they might behave as low molecular weight species, thereby easing the processability of these polymers. In addition, if there is stacking of the PcM rings in the solid state, the polymers possessing the PcM rings might have some electronic conductivity. Furthermore, because of the high thermal stabilities of the poly(aryl ether sulfone)s and the PcM rings, these polymers could be used in high temperature applications.

7.3. Synthesis and characterization of metallophthalocyanine end-capped polymers

Poly(aryl ether sulfone)s end-capped with o-phthalonitrile groups were synthesized as precursors to phthalocyanine end-capped polymers following procedures described by Keller.¹⁷ In the first step, a low molecular weight poly(aryl ether sulfone) was synthesized by reaction of bis(4-fluorophenyl)sulfone with an excess of BPA in a DMAc/toluene solvent system. The temperature of the reaction flask was maintained at 135 °C for 2-3 hours in order to remove all the water azeotropically with toluene from the reaction mixture. The flask temperature was then increased to 160 °C and the reaction mixture stirred at this temperature for another 3 hours to obtain polymers with phenoxide end-groups. At this juncture, the temperature of the flask was lowered to 50 °C and excess 4-nitrophthalonitrile was added. The reaction temperature was raised to 115-20 °C after the addition and maintained at this temperature for 4 hours according to a procedure described by Keller.¹⁷ This is described in scheme 7.1. Polymers of different average molecular weights were synthesized by following this procedure.



Scheme 7.1 Synthetic route to poly(ether sulfone)s end-capped with metallo phthalocyanines

Metallophthalocyanine end-capped poly(aryl ether sulfone)s were synthesized from the o-phthalonitrile end-capped polymers by reacting them with excess phthalonitrile and metal salt/metal in quinoline at high temperatures (Scheme 7.1). A large excess of phthalonitrile was used in order to achieve as complete conversion as possible of phthalonitrile end-groups to phthalocyanines and to reduce the extent of chain extension or cross-linking caused by having phthalocyanine moieties attached to different polymer chains.

The ¹H NMR spectrum of a poly(aryl ether sulfone) with DP = 20 is shown in Figure 7.1. This is similar to the spectrum observed by McGrath et al¹⁹ previously. There is no signal observed between 7.35 and 7.75 ppm in this spectrum. Figure 7.2 represents the ¹H NMR spectrum of the o-phthalonitrile end-capped poly(aryl ether sulfone) with

DP=20. Proton H_B which is in the vicinity of a -CN group appears as a doublet at 7.72 ppm whereas proton H_A appears as a doublet of doublet around 7.39 ppm because of meta coupling with the H_C proton.



Figure 7.1. ¹H NMR of poly(aryl ether sulfone)s (DP=20)

The H_c proton, in turn, appears as a doublet at around 7.48 ppm. From the NMR integration it is estimated that the end-capping of the polymer chains by phthalonitrile groups is quantitative.



Figure 7.2. ¹H NMR of poly(aryl ether sulfone)s end-capped with o-phthalonitriles



Figure 7.3. IR spectra of o-phthalonitrile and PcM end-capped poly(aryl ether sulfone)s

The presence of -CN groups in the polymer is further confirmed by a strong absorption band at 2240 cm⁻¹ (Figure 7.3) in the IR spectrum. The conversion of o-phthalonitrile end

groups to metallophthalocyanine groups is confirmed by the disappearance of the -CN absorption band in the PcM end-capped polymers as shown in Figure 7.3.



Figure 7.4. UV-VIS spectrum of CuPc end-capped poly(aryl ether sulfone)s

The appearance of an absorption maximum at 674 nm (Figure 7.4) is another evidence of the presence of PcM moieties in the CuPc end-capped poly(aryl ether sulfone)s. Similarly, FePc end-capped poly(aryl ether sulfone)s showed an absorption maximum at 656 nm in the UV-VIS spectrum (Figure 7.5).

The GPC spectra of the o-phthalonitrile and CuPc end-capped poly(aryl ether sulfone)s are presented in Figure 7.6. In the case of PcM end-capped polymers, a shoulder in the higher molecular weight region is observed. This is presumably due to some chain extension caused by the reactions of phthalonitriles of different polymer chains to form phthalocyanines. A similar GPC pattern was observed earlier by Hay et al ¹⁴ for poly(aryl ether)s containing tetrapyrazineporphyrazine units.



Figure 7.5. UV-VIS spectrum of FePc end-capped poly(aryl ether sulfone)s



Figure 7.6. GPC spectra of o-phthalonitrile and PcM end-capped poly(aryl ether sulfone)s

7.4. Properties of PcM end-capped polymers

Poly(aryl ether sulfone)s with PcM end groups were synthesized with different degrees of polymerization in order to evaluate the effect of PcM rings on the physical properties of polymers and also to probe if there is any stacking between the PcM rings in the solid state. Physical properties of CuPc end-capped polymers with DP=20 and DP=50 are presented in Table 7.1.

Number of repeat units	Molecular Weights	T _g (°C)
20	M _n =8, 000 M _w =18, 000	162
20 with phthalocyanine end caps	M _n =14, 000 M _w =39, 000	190
50	M _n =22, 000 M _w =33, 000	187
50 with phthalocyanine end caps	M _n =21, 000 M _w =61, 000	197

	Table 7.1.	Physical	properties of	CuPc end-cap	pped poly	y(aryl eth	ner sulfone)
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The increase in M_w values for CuPc end-capped polymers is reminiscent of the chain extension which occured in solution during the PcM ring formation as described earlier.¹⁴ An increase of 30 °C in T_g for polymers (DP=20) with CuPc rings is perhaps due to a higher concentration of phthalocyanine rings in these polymers. In the solid state there is probably some aggregation of the PcM rings in these polymers which enhances the T_g . The higher the average molecular weight of the polymer, the lower is the amount of Pc rings in the polymer with a resulting smaller effect on T_g . This is clearly noticeable in the case of polymers with DP=50. The increase in T_g for these Pc end-capped polymers compared to the o-phthalonitrile end-capped precursors is only 10 °C which could be accounted for by a bulky end group with no stacking.

To further understand the effect of PcM rings on the polymer properties in the solid state, annealing studies were carried out on some of the polymers possessing higher concentrations of PcM moieties. In the annealing studies, the polymer sample was continuously heated at a temperature approximately 50 °C above its T_g , for 12 h under a nitrogen atmosphere. The thermal profiles of a poly(aryl ether sulfone) with FePc end

groups (DP=20) before and after annealing, are presented in Figure 7.7 and Figure 7.8, respectively.



Figure 7.7. DSC of FePc end-capped poly(aryl ether sulfone)s before annealing



Figure 7.8. DSC of FePc end-capped poly(aryl ether sulfone)s after annealing

The T_g of the FePc end-capped poly(aryl ether sulfone) before annealing is 175 °C. It is evident from Figure 7.8 that after annealing there is a melting endotherm at around 240 °C in addition to increased T_g at 190 °C. In the melt state, because of the mobility of the polymer chains, there is a distinct possibility that the PcM rings would aggregate and stack because of the presence of weak intermolecular interactions. This would give rise to crystallization in the stacked domains of the polymer chains. The presence of a melting endotherm, therefore, may be indicative of some stacking of Pc end groups in these polymers. Also the increase in T_g in these polymers and in the polymers containing CuPc end-groups is most likely due to stacking of PcM rings in the solid state.

7.5. Conclusions

PcM end-capped poly(aryl ether sulfone)s were synthesized from the ophthalonitrile end-capped polymers in reasonably good yield. The polymers were soluble in common organic solvents. PcM end-capped polymers showed increased T_g which is probably due to stacking of PcM moieties. A melting endotherm due to crystallization presumably caused by stacking of PcM rings, was observed after annealing.

7.6. Experimental section

Materials

4,4'-Isopropylidenebiphenol (BPA) (Aldrich; 99+%), bis(4-fluorophenyl)sulfone (Aldrich; 99%), 4-nitrophthalonitrile (Aldrich; 99%), phthalonitrile (Aldrich; 98%), copper chloride (Lancaster; 97%), iron powder (Aldrich; 99.99%) were used as received. The solvents were used as received from Lancaster.

Characterization techniques

NMR spectra were recorded on a Varian Unity 500 spectrometer. The GPC analyses were carried out on a Waters 510 HPLC using four phenogel 5μ m columns arranged in series. Chloroform was used as eluent and the uv detector was set at 254 nm. Infrared spectra were taken using an Analect FT-IR AQS-20 spectrometer. UV-VIS spectra were recorded on a Hewlett Packard 8452A diode array spectrophotometer. A

Seiko 220 DSC and a 220 TG/DTA instrument were used for the thermal analyses of the polymers under nitrogen atmosphere. The heating rate in both cases was 20 °C/min.

General procedure for the synthesis of o-phthalonitrile end-capped poly(aryl ether sulfone)s

To a 50 mL three-necked round-bottomed flask equipped with a Dean-Stark trap, condenser, thermometer, and nitrogen inlet, were added BPA (2.3970 g, 10.5 mmol), bis (4-fluorophenyl)sulfone (2.5425 g, 10 mmol), anhydrous potassium carbonate (1.9 g, 13.75 mmol), 22 mL of N, N'-dimethylacetamide (DMAc), and 11 mL of toluene. The reaction flask was purged with nitrogen for about fifteen minutes. The flask was then heated to 140 °C under nitrogen atmosphere and maintained at this temperature for two and a half h in order to azeotropically remove all the water from the reaction mixture. The temperature of the reaction mixture was then increased to 160 °C and held at this temperature for 4 h. The reaction mixture was then cooled down to room temperature. At this juncture, 4-nitrophthalonitrile (1.73 g, 10 mmol) was added to the reaction flask and the temperature was raised to 120 °C. The reaction flask was maintained at this temperature for another 4 h and then cooled down. The mixture was diluted with more DMAc and then precipitated into a 2/1 mixture of methanol and water. The pale yellow polymer was redissolved in chloroform and filtered hot through a bed of celite in order to remove inorganic salts. The chloroform solution was concentrated and reprecipitated again into a mixture of 400 mL of methanol and 200 mL of water. The final polymer was dried in vacuo at 120 °C for 48 h. The yield of the polymer was 96%.

General procedure for the synthesis of metallophthalocyanine end-capped poly(aryl ether sulfone)s

To a 50 mL three-necked round-bottom flask equipped with a reflux condenser and a nitrogen inlet were added o-phthalonitrile end-capped polymer (0.8 g), phthalonitrile (0.6 g, 30 equiv based on the polymer), copper (II) chloride (0.3 g, 15 equiv based on the polymer) and 15 mL of quinoline. The reaction mixture was heated at 220-230 $^{\circ}$ C under

nitrogen atmosphere for about 3 h during which time it turned dark blue. Some insoluble dark blue solids were observed, due to the formation of free copper-phthalocyanine molecules in the reaction mixture. The solution was cooled down at the end of the reaction and precipitated into 500 mL of methanol. The dark blue polymer was washed with acetone and ethanol and then soxhlet extracted with chloroform to separate it from metal-phthalocyanine impurities. The concentrated chloroform solution of the polymer was precipitated again into 500 mL of methanol. The blue fibrous polymer was then dried *in vacuo* at 120 $^{\circ}$ C for 24 h. The final yield of the polymer was 40%.

The above procedure was repeated for iron-phthalocyanine end-capped poly(aryl ether sulfone)s except in this case iron powder was used instead of copper (II) chloride. The isolated yield of the polymer was again about 40%.

7.7. References and notes

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Contributions to Original knowledge

This thesis describes the convenient syntheses of novel classes of polycyclic structures as precursors to thermosetting resins.

We discovered for the first time that when xylene was used as a solvent in the condensation of phenol and formaldehyde using sulfuric acid catalyst to prepare novolac type resin, m-xylene was incorporated as an end group in the phenol-formaldehyde oligomers. Matrix Assisted Laser Desorption Ionization-Time of Flight Mass Spectrometry characterization clearly demonstrated the presence of xylene end-capped units by displaying the masses of each unit. These series of oligomers have also been thoroughly characterized by using other analytical techniques such as NMR, Gradient HPLC, GPC etc. This led us to develop a new method of synthesis of p-substituted phenol-formaldehyde novolac type resins by using cation-exchange resin as acid catalyst in the presence of an inert solvent such as chlorobenzene.

Three novel classes of polycyclics, namely, oligomeric polycyclic carbonates, phosphonates and siloxanes were then synthesized by reacting p-substitued phenol-formaldehyde resins with the corresponding dihalo compounds under high dilution conditions.

All three classes of polycyclic precursors underwent a series of novel ring-opening polymerizations when heated at elevated temperatures in the presence of initiators. This resulted in three new categories of thermoset materials with potentially useful properties. The cross-linked polyphosphonates imparted good flame retardant properties to the final product. When polycyclic siloxanes were mixed with a commercial co-polymer gum and cross-linked at elevated temperature, they provided excellent thermal stability to the resultant gum mixture. A novel Bisphenol A dimer was synthesized by a one step reaction by reacting excess BPA with formaldehyde in the presence of cation exchange resin. This was then used as a starting material to synthesize three novel classes of oligomeric polycyclics under high dilution conditions. These polycyclic precursors had low melting points and therefore could potentially be used as precursors to thermosetting materials. Full characterizations of these polycyclics were carried out using MALDI-TOF MS, Gradient HPLC and NMR.

The dimer also co-polymerized well with BPA and triphosgene to produce a series of co-polycarbonates with internal cyclic carbonate moieties on the backbone. In addition, a novel method was developed to co-polymerize the dimer with BPA and triphosgene *in situ*. These internal cyclic carbonates underwent ring-opening polymerizations when subjected to thermal curing at elevated temperatures.

A series of low molecular weight poly(aryl ether sulfone)s with metalphthalocyanine end-groups were synthesized to improve the processability of these polymers and also to investigate the stacking phenomena of the phthalocyanine rings in the melt.