Synthesis and Characterization of
New Polycarbonate Material Systems

by

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(Abstract)

Bisphenol A polycarbonate is an engineering thermosplastic which can be utilized for a variety of applications. Modifications to improve upon the properties of this useful material have been attempted since its invention. Three modifications of bisphenol A polycarbonate and its copolymers have been examined in this work.

The hydrolytic stability of copolymers of polydimethylsiloxane and polycarbonate was improved by the synthesis of pre-formed phenol functional polydimethylsiloxane oligomers in which the Si is attached directly to the aromatic ring of the hydroxyaryl functional component. In situ random block copolymers of polydimethylsiloxane and polycarbonate were synthesized by interfacial polymerization techniques. The Si—aryl bonds of the novel polydimethylsiloxane oligomers were found to impart good thermal and hydrolytic stability to the random block copolymers.

Terminally reactive polycarbonate oligomers were also synthesized in order to form polycarbonate network materials. 4-Acetoxy styrene was utilized as a stable precursor to 4-vinylphenol which could then be used to quantitatively control the molecular weight and functionality of the polycarbonate chains. The
reactive oligomers were found to undergo a thermal cure above the respective glass transition temperatures to form insoluble networks. These network materials were found to have superior solvent resistance as compared to the linear material while retaining much of the useful mechanical properties (high fracture toughness, etc.) of bisphenol A polycarbonate. Furthermore, the glass transition temperatures of the networks were found to increase with a decrease in the molecular weight between crosslinks.

The fire resistance properties of polycarbonate were modified by the copolymerization of bisphenol A with phenol derivatives of triphenylphosphine oxide. The effect of changes in the composition were determined by differential scanning calorimetry and thermogravimetric analysis. The glass transition temperature, as well as the residual char yield at elevated temperatures was found to increase with an increase in the phosphorus monomer content as measured by the two respective methods. Cone calorimetry was also performed on the samples to determine the heat release rate, which reflected an increase in the fire resistance properties with an increase in the phosphorus content.
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1.0 INTRODUCTION

Polycarbonates have become a very important class of polymeric materials since their invention in the mid 1950's.\textsuperscript{1,2} Although the term "polycarbonate" can be used to refer to any polymer, aliphatic or aromatic, with the repeating — O—C(O)—O — unit, it has most often come to be used to refer to the specific polymer derived from 2,2-bis(4-hydroxyphenyl)propane (bisphenol A) (Figure 1.1). The formal IUPAC name for this material is poly(oxy-1,4-phenylenedimethylmethylene-1,4-phenylenedioxy carbonyl). This is the polycarbonate material which is produced worldwide to total more than a billion pounds per year.\textsuperscript{3}

![Figure 1.1 Bisphenol A Polycarbonate Repeat Unit](image-url)

The polycarbonate derived from bisphenol A is classified as an engineering thermoplastic and has desirable physical properties which allow for its use in a wide number of applications. Representative physical properties for Lexan polycarbonate are listed in Table 1.1.
Table 1.1 Representative Physical Properties of Bisphenol A Polycarbonate (Lexan)\(^4\)

<table>
<thead>
<tr>
<th>PROPERTY</th>
<th>ENG(SI) UNITS</th>
<th>TEST METHOD</th>
<th>VALUE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Specific Gravity</td>
<td>lb/in(^3) (g/cm(^3))</td>
<td>ASTM D 792</td>
<td>1.20</td>
</tr>
<tr>
<td>Water Absorption</td>
<td>%</td>
<td>ASTM D 570</td>
<td>0.35</td>
</tr>
<tr>
<td>(equilib. 23°C)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tensile Strength</td>
<td>psi(MPa)</td>
<td>ASTM D 638</td>
<td>10000 (70)</td>
</tr>
<tr>
<td>(break, type 1, 0.125in (3.2 mm))</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tensile Elongation</td>
<td>%</td>
<td>ASTM D 638</td>
<td>125-135</td>
</tr>
<tr>
<td>(break, Type 1, 0.125in (3.2 mm))</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Compressive Strength</td>
<td>psi(MPa)</td>
<td>ASTM D 695</td>
<td>12500(86)</td>
</tr>
<tr>
<td>Tensile Modulus</td>
<td>lb/in2 X 10(^3)</td>
<td>ASTM D 638</td>
<td>350</td>
</tr>
<tr>
<td>Hardness</td>
<td>—</td>
<td>ASTM D 785</td>
<td>118</td>
</tr>
<tr>
<td>(Rockwell R)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Izod Impact</td>
<td>ft-lb/in(J/m)</td>
<td>ASTM D 256</td>
<td>13-18(694-961)</td>
</tr>
<tr>
<td>(notched, 0.125in (3.2mm), 23°C)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Vicat Softening Temp.</td>
<td>°F(°C)</td>
<td>ASTM D 648</td>
<td>310(154)</td>
</tr>
<tr>
<td>UL94V-2 Flame Class Rating</td>
<td>in(mm)</td>
<td>UL 94</td>
<td>0.062(1.57)</td>
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</tbody>
</table>

\(^4\)
Although bisphenol A polycarbonate has many useful properties, it is most noted for its exceptional impact strength. This characteristic has led to many applications up to and including its use as a bullet proof material. The origin of its exceptional impact strength is widely debated, but most evidence suggests the ability of this material to undergo segmental motion at temperatures well below the glass transition temperature.

Although many of the physical properties of this material are excellent, research has persisted in attempts to improve upon this material. One of the largest drawbacks of this material is its poor solvent resistance. The amorphous nature of the material allows it to be soluble in a number of organic solvents. Although this feature allows the material to be conveniently processed from solution, it is a problem in applications where solvent exposure is possible such as in automotive uses. Improving upon this property while maintaining others has been very difficult to achieve.

A major objective of much of the research in this thesis has been to identify feasible approaches toward improving the properties of this already versatile material. The synthesis of new copolymers or network structures from terminally reactive materials has permitted specific properties to be modified while essentially maintaining other valuable physical characteristics. Specific areas of improvement have concentrated on improving impact toughness properties through polydimethylsiloxane block incorporation while generating more hydrolytically stable linkages between blocks. Improving the fire resistance properties through the incorporation of an inherently fire resistant phosphorus containing comonomer has been researched. Improvement of solvent resistance properties was also achieved through the synthesis of terminally
reactive oligomers which could be used to generate insoluble network structures.

The review of the pertinent literature will particularly concentrate on specific areas related to the thesis objectives rather than on a general overview of the classes of materials investigated. The literature review is thus not intended to be exhaustive, but rather to reference some of the work that has been done in the particular areas and to guide the interested reader toward more information on the subject. Excellent reviews of polycarbonates have recently been published, and these should be consulted for more information. The synthesis of polycarbonates will be presented as well as other information related to this work.

Since an effort was made to incorporate polydimethylsiloxane blocks into polycarbonate copolymers, some review of siloxane chemistry will be presented. However, only a brief discussion of the general class of polyorganosiloxanes will be presented, as more detailed discussions are available in various books, reviews, and dissertations from this research group. The review will concentrate more on functionalized polydimethylsiloxane oligomers and their incorporation into block copolymers (specifically polycarbonates). Although an excellent review of functionalized polydimethylsiloxanes has been done, new information including the specific chemistry related to the incorporation of the blocks will be described.

The second specific area of interest will deal with functionalized polycarbonates. Since the research presented in this thesis deals with telechelic reactive polycarbonates and their subsequent reaction to form network structures, relevant literature in this area will be reviewed.
The fire resistant properties of polycarbonates and methods of increasing this property will also be briefly discussed. This will include the use of additives as well as comonomers which have been incorporated into the polymer backbone. Phosphorus containing compounds will be a major focus, but comparisons with other fire retardant species will be included.

This selective review of the literature will then be followed with the experimental research studies conducted in these three areas. The results will then be discussed so as to compare and contrast the new materials with those previously investigated.
2.0 BACKGROUND

2.1 Polycarbonates

2.1.1 Historical Development

Early polymerization experiments to synthesize aromatic polycarbonates were carried out by Einhorn in 1898\(^{18}\) and by Bischoff and von Hedenstroem in 1902.\(^{19}\) These workers attempted to synthesize polycarbonates based on resorcinol and hydroquinone by reaction with phosgene in pyridine solution and by melt transesterification with diphenylcarbonate, respectively. The polymers obtained were insoluble and of low molecular weight. Aromatic polycarbonates were not investigated again until the mid 1950's when Schnell and coworkers at Farbenfabriken Bayer A.G. (now Bayer AG) successfully synthesized aromatic polycarbonates based on bis(4-hydroxyphenyl)alkanes.\(^{1}\) Fox at General Electric was also investigating these types of polymers and had also discovered their useful properties.\(^{2}\) Both companies quickly began commercial production of the polycarbonate based on 2,2-bis(4-hydroxyphenyl)propane (bisphenol A) by their respective processes.\(^{20,21}\) At the same time, researchers at Eastman Kodak were investigating aromatic-aliphatic polymers based also on bisphenol A.\(^{22}\) Although General Electric and Bayer AG (as well as its subsidiary Mobay, now Miles) were initially the two major world producers of polycarbonate, other companies such as the Dow Chemical Company have also become major producers of this engineering thermoplastic.
2.1.2 Synthetic Methods

Since their introduction, aromatic polycarbonates have traditionally been synthesized by three different methods, similar to other polyesters. These methods of synthesis are 1) solution, 2) melt transesterification, and 3) phase transfer catalyzed interfacial reactions. To these three general methods must now be added the technique of anionic ring opening of cyclic oligomers. Although this method had been recognized from early on,\textsuperscript{23} and is used extensively for the polymerization of cyclic aliphatic carbonates, it has only achieved importance in the past decade through the work of researchers at General Electric.\textsuperscript{24-30} Solid state polymerization is yet another method of synthesis which is now of importance. This is a recent improvement on the melt transesterification reaction and can be included in that category. Other innovative procedures such as catalyzed reactions of bisphenols with carbon monoxide have to date achieved little success, but have no doubt been worth investigation.

2.1.2.1 Interfacial Polymerization

Schnell's early work dealt predominately with the synthesis of polycarbonates via interfacial methods.\textsuperscript{1} This method has also become the most important synthetic method for the industrial production of polycarbonates. The alkali salts of aromatic dihydroxy compounds react readily with phosgene in aqueous solutions to form aryl chlorocarbonic ester groups (chloroformates). These chlorocarbonic ester groups then react relatively slowly with additional alkali phenolates at room temperature. Hydrolysis of the chlorocarbonic ester
groups is also rather slow under these conditions. This approach thus yields only low molecular weight oligomers with chlorocarbonic ester end groups.

The first experiments by Schnell consisted of introducing gaseous phosgene into a stirred two phase mixture of xylenes and an alkaline solution of bisphenol A.¹ Since the resulting polymer was not soluble in the organic solvent utilized, the polycarbonate precipitated from the reaction mixture. Modest molecular weights were obtained since the xylenes were able to swell the polymer enough for the reaction to take place to some extent.

Much better results are obtained when a solvent that dissolves both the phosgene and the resulting polymer is used. Chlorinated aliphatic solvents have been found to work well, with methylene chloride being the most widely used solvent. The formation of high molecular weight polycarbonates is still difficult under these conditions. Although low molecular weight chloroformate terminated carbonate oligomers are formed relatively quickly, polycondensation is rather slow without added catalyst.³¹ Bottenbruch and Schnell found that when catalytic amounts of tertiary amines or quaternary ammonium salts were added to the reaction mixture the polycondensation was much faster.¹ The action of the tertiary amines and the quaternary ammonium salts has been found to be quite different.³¹

The tertiary amine reacts with the chloroformate to form an acyl ammonium salt. This acyl ammonium salt is much more reactive towards the alkali phenolate than is the chloroformate itself. Reaction with the alkali phenolate forms a carbonate group and regenerates the tertiary amine. The acyl ammonium salt is also more reactive towards hydrolysis than the chloroformate.
Hydrolysis also regenerates the tertiary amine as well as a phenolate (Scheme 2.1.2.1.1).

Scheme 2.1.2.1.1 Trialkylamine Catalyzed Reactions During Polycarbonate Formation
The competition between these two reactions, condensation and hydrolysis, determines the rate of the reaction, as well as the final molecular weight obtained. The rates for these two reactions are very different for different tertiary amines. These competitive reaction rates have been studied recently for a variety of tertiary amines and quaternary ammonium compounds.\textsuperscript{32} The relative rates for the formation of diphenylcarbonate from phenylchloroformate using different amine catalysts is shown in Table 2.1.2.1.1. The reactivity of the bisphenol also affects these competitive reactions.\textsuperscript{31}

The use of quaternary ammonium salts has also been utilized to catalyze the polycondensation reaction. The quaternary ammonium salt phase transfer catalyst can exchange with the cation of the alkali phenolate to form a quaternary ammonium phenolate salt. This increases the rate of the reaction since this more hydrophobic group can now migrate to the organic layer and react with phosgene or chloroformate groups on growing chains\textsuperscript{33} (Scheme 2.1.2.1.2).
Table 2.1.2.1.1 Influence of Amine Structure on the Rates of Hydrolysis and Condensation Reactions of Phenylchloroformate

<table>
<thead>
<tr>
<th>Amine</th>
<th>Reaction Time</th>
<th>Residual Phenyl Chloroformate</th>
<th>Diphenyl Carbonate Product</th>
<th>Relative Rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Et₃N⁵</td>
<td>30 s</td>
<td>80</td>
<td>20</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>2 min.</td>
<td>60</td>
<td>40</td>
<td></td>
</tr>
<tr>
<td></td>
<td>10 min.</td>
<td>0</td>
<td>99</td>
<td></td>
</tr>
<tr>
<td>Me₂NBu⁵</td>
<td>30 s</td>
<td>38</td>
<td>55</td>
<td>5</td>
</tr>
<tr>
<td></td>
<td>2 min.</td>
<td>7</td>
<td>85</td>
<td></td>
</tr>
<tr>
<td></td>
<td>3 min.</td>
<td>0</td>
<td>90</td>
<td></td>
</tr>
<tr>
<td>Bu₄NOH⁶</td>
<td>25 min.</td>
<td>92</td>
<td>8</td>
<td>0.007</td>
</tr>
<tr>
<td>(i-Pr)₂NEt⁷</td>
<td>25 min.</td>
<td>95</td>
<td>5</td>
<td>0.005</td>
</tr>
<tr>
<td>Pyridine⁸</td>
<td>1 min.</td>
<td>85</td>
<td>5.5</td>
<td>0.35</td>
</tr>
<tr>
<td></td>
<td>5 min.</td>
<td>56</td>
<td>16</td>
<td></td>
</tr>
<tr>
<td></td>
<td>10 min.</td>
<td>25</td>
<td>27</td>
<td></td>
</tr>
<tr>
<td>Et₃N⁹</td>
<td>10 s</td>
<td>31</td>
<td>68</td>
<td>8.5</td>
</tr>
<tr>
<td></td>
<td>30 s</td>
<td>1</td>
<td>99</td>
<td></td>
</tr>
<tr>
<td>Et₃NC</td>
<td>30 s</td>
<td>40</td>
<td>60</td>
<td>1.9</td>
</tr>
<tr>
<td></td>
<td>2 min.</td>
<td>8</td>
<td>91</td>
<td></td>
</tr>
<tr>
<td></td>
<td>5 min.</td>
<td>0</td>
<td>99</td>
<td></td>
</tr>
</tbody>
</table>

²0.0 mmol of phenylchloroformate was added to 0.20 mmol of catalyst rapidly stirred in 40 ml CH₂Cl₂ and 2.5 ml of 2.0 M NaOH. ²²1 mmol of catalyst with 2.5 ml of 2.0 M NaOH. ²²1 mmol of catalyst with 10 mmol of water.
Scheme 2.1.2.1.2 Action of Tetraalkylammonium Phase Transfer Catalyst on the Interfacial Polycarbonate Reaction

Many variables govern the kinetics of interfacial reaction systems. Some of these variables include stirring speed, reaction temperature, nature of the dihydroxy compound, solvent, concentration in both phases, ionic strength, catalyst concentration, pH of the reaction mixture, as well as other factors such as phosgene addition rate. Other variables which are even harder to define also play a role in this type of reaction. Some of these are surface factors which influence the nature of the phases such as the total surface area, drop size,
drop distribution, etc. The intermediates which are formed during the polycondensation can also have an effect on the reaction as the oligocarbonates can affect the phase distribution. The chloroformate and phenolate terminated oligomers formed during the reaction have an emulsifying effect on the two phase reaction. Since the oligomers are changing throughout the polymerization, this is a complicated variable. The intentional addition of emulsifiers is another way to affect the phase distribution. The results obtained when emulsifiers are added are complex and depend on the solvent and other components as competing hydrolysis reactions affect both the yield and molecular weight. It becomes easy to see that these polymerizations are very complex and are still not completely understood.

Stirring speed is one variable which can be controlled and possibly eliminated. Through experimental results Smirnova et al. concluded that above stirring rates of 4000 rpm the formation of the polycarbonate changes from a diffusion controlled process to that of a kinetically controlled reaction. This should also depend on the reaction vessel configuration.

Rather than using phosgene in the polycondensation, the preformed bischlororcarbolic ester (bischloroformate) can be reacted with the aromatic dihydroxy compound to form the polycarbonate. The major benefit of this type of reaction is that alternating copolymers can be synthesized (Scheme 2.1.2.1.3). Although, under interfacial conditions (especially with the use of a catalyst) some hydrolysis does occur to both limit the molecular weights and disrupt the alternation. Block copolymers can also be synthesized by forming oligomeric bischloroformates and reacting this with any hydroxyl terminated oligomer. General Electric has used this method in synthesizing
poly(carbonate-co-dimethylsiloxane)s.\textsuperscript{37,38} This particular application of this technique will be discussed further in section 2.2.4.

\[
\text{HO-R-OH} + \text{Cl-C-O-} \underset{\text{HO}}{\text{C}} \underset{\text{O}}{\text{O}} \underset{\text{O}}{\text{C}} \underset{\text{Cl}}{\text{O}} \\
\downarrow \quad \text{H}_2\text{O} \quad \text{CH}_2\text{Cl}_2 \\
\quad \text{NaOH} \\
\text{ } \underset{\text{O}}{\text{O}} \underset{\text{C}}{\text{O}} \underset{\text{O}}{\text{C}} \underset{\text{O}}{\text{O}} \underset{\text{O}}{\text{C}} \underset{\text{C}}{\text{O}}
\]

\textbf{Scheme 2.1.2.1.3 Synthesis of Alternating Polycarbonates via Bischloroformate of Bisphenol A}

2.1.2.2 Solution Polymerization

The solution method of polymerization was the first industrial method for the production of bisphenol A polycarbonate employed by the General Electric Company.\textsuperscript{21} The polymerization is typically conducted in dry pyridine with or without a cosolvent. Phosgene is introduced into the solution of the aromatic dihydroxy compound forming an adduct with the pyridine which is much more reactive towards the bisphenol.\textsuperscript{39} Molecular weight is increased through the reaction of more bisphenol with the acyl pyridinium salt end groups (Scheme 2.1.2.2.1). Although some polycarbonates are soluble in pyridine itself, usually a cosolvent capable of dissolving the resulting polycarbonate is required.
Scheme 2.1.2.2.1 Participation of Pyridine in Solution Polycarbonate Synthesis

The solution method works well for the synthesis of copolymers utilizing the preformed bischloroformates of particular monomers or oligomers. Relative to the interfacial approach, more perfectly alternating structures can be synthesized, since the hydrolysis can be reduced by the rigorous exclusion of water. Controlled molecular weight, hydroxy functional oligomers can also be synthesized by offsetting the stoichiometry. This technique also allows
various hydrolyzable endgroups to be incorporated to ultimately obtain hydroxy functional oligomers with better molecular weight control.\textsuperscript{13,40}

However, on an industrial scale, this synthetic method has many difficulties associated with it. The quantitative removal of pyridine and pyridinium salts from the isolated product is difficult, as is the separation and recycling of the mixed solvents.\textsuperscript{39} Today, this method is mostly utilized only on a laboratory scale.

\textbf{2.1.2.3 Melt Transesterification}

The melt transesterification reaction is becoming an important route to the synthesis of polycarbonates. This method was first used by Bischoff and von Hedenstroem in 1902.\textsuperscript{19} Fox used this method when first synthesizing the polycarbonate of bisphenol A at the General Electric Laboratories. The transesterification of an aromatic dihydroxy compound with a diaryl carbonate can be accomplished at elevated temperatures, and is accelerated by a variety of basic catalysts (Scheme 2.1.2.3.1). The development of this method has been slow because of the many problems associated with it, as discussed in the following pages.\textsuperscript{39}
Scheme 2.1.2.3.1 Melt Transesterification Synthesis of Polycarbonate

The polycarbonate obtained from this method can be highly colored due to the side reactions which can take place. For example, the thermal instability of the bis(4-hydroxyphenyl)alkanes can lead to side reactions of the Kolbe-Schmitt type. Bisphenol A itself is cracked to phenol and isopropenylphenol at temperatures above 150° C in the presence of alkali. The free hydroxyl groups are considered to be responsible for this instability, and accordingly this
side reaction can be decreased by performing the reaction in a two step sequence.\textsuperscript{39} In the first step, an excess of diphenyl carbonate is reacted with the dihydroxy monomer in the presence of a basic catalyst at temperatures between 150 and 200°C. This yields low molecular weight, phenylcarbonte terminated polycarbonates. At much higher temperatures (greater than 250°C) and reduced pressures, diphenyl carbonate is eliminated and the reaction can be pushed to yield high molecular weight materials. The catalyst is much more effective in the first step than in the second step where diphenyl carbonate is eliminated.\textsuperscript{39,42}

Other side reactions such as the rearrangement shown in Scheme 2.1.2.3.2 can still take place at these elevated temperatures.\textsuperscript{39} These side reactions lead to colored products and can also cause crosslinking and branching reactions. Much work has gone into development of the proper catalysts and conditions which can avoid these side reactions.\textsuperscript{3,42-44}

\[
\begin{array}{c}
\text{O} \quad \text{O} \\
\text{[O- \text{C-O-} \text{C-O]} -} \\
\text{> 150°C} \\
\text{OH}^- \\
\text{[O- \text{C-O-} \text{COOH]} -}
\end{array}
\]

**Scheme 2.1.2.3.2** Kolbe-Schmitt Type Rearrangement During Base Catalyzed Melt Transesterification Synthesis of Bisphenol A Polycarbonate
The melt transesterification reaction thus requires elevated temperatures and high vacuum for removal of phenol and diphenyl carbonate from the viscous melt in order to achieve high molecular weight polycarbonate. Furthermore, the polycarbonates tend to have a very high melt viscosity so that the synthesis of high molecular weight material by this method is rather difficult and requires special equipment. The control of the molecular weight and the end groups is also not as easy to regulate as in the other processes. In fact, the reaction often yields a polymer which can continue to chain extend upon further heating.

There are benefits to the synthesis of the polycarbonates by this method. The use of solvents as well as the washing steps and waste water can be eliminated. This method also has the potential to be a phosgene-free process if the use of phosgene for the synthesis of the diphenyl carbonate starting material is eliminated. This will be discussed further in section 2.1.2.5. The isolation of the polymer is also simplified as it can be directly extruded from the reactor.

A relatively new technique of solid state polymerization can be included in this category. The method of solid state polymerization of crystalline polyesters and polyamides has been known for some time, and is used industrially to obtain high molecular weight poly(ethylene terephthalate), poly(butylene terephthalate), as well as nylon-6 and nylon-6,6 from low molecular weight crystalline prepolymer. The technique involves heating the crystalline prepolymer slightly below the melting temperature ($T_M$), but above the $T_g$, under vacuum to effect chain extension in the solid state. The benefit of this type of reaction method is that high molecular weight materials can be
synthesized which could not be synthesized by conventional melt polymerization techniques because of their high melt viscosities. This technique has been applied to aromatic polycarbonates only recently.\textsuperscript{3,46}

The polycarbonate of bisphenol A as well as other polycarbonates are known to crystallize under the influence of solvent.\textsuperscript{5} This allows one to obtain crystalline oligomers which can then be reacted to form high molecular weight materials in the solid state.

One of the other benefits of this type of reaction is that low molecular weight oligomers can be synthesized by a variety of methods including methods which do not normally lead to high molecular weight materials. The melt transesterification reaction between bisphenol A and dimethyl carbonate, or the mono or dimethyl carbonate of bisphenol A are such reactions.\textsuperscript{47,48} The crystallized oligomers which can be obtained can then be made to react to high molecular weight polymers through solid-state techniques.

\textbf{2.1.2.4 Macrocyclic Formation and Ring Opening Polymerization}

Early in the development of polycarbonate polymerization, it was observed that the interfacial and solution syntheses yielded cyclic oligomers.\textsuperscript{23} Under the proper dilution conditions and reaction of bisphenol A with the preformed bischloroformate of bisphenol A, low yields (21\%) of the cyclic tetramer (Figure 2.1.2.4.1) could be obtained. It was found that this cyclic oligomer could be polymerized to very high molecular weight linear polycarbonate in the melt utilizing various alkaline catalysts. The industrial exploitation of this technique did not occur because of the low yield of oligomers obtained as well as the high processing temperatures required to melt the cyclic tetramer. Some later work
indicated that very large rings with molecular weights as high as 15,000 - 30,000 could be obtained under the proper conditions by the combined condensation/hydrolysis reaction of bisphenol A bischloroformate with triethylamine catalyst.\textsuperscript{49} The materials produced showed a deficiency of end groups, which could be generated through a controlled saponification with piperdine. The resulting linear materials showed an increase in viscosity while the number average molecular molecular weights did not change.

![Cyclic Tetramer of Bisphenol A](image)

**Figure 2.1.2.4.1** Cyclic Tetramer of Bisphenol A

Researchers at General Electric found that they could obtain very high yields of cyclic oligomers by the slow addition of a solution of bisphenol A bischloroformate to a rapidly stirred mixture of methylene chloride, aqueous sodium hydroxide, and triethylamine.\textsuperscript{24-30} Under the proper conditions, the formation of linear oligomers was excluded and a mixture of cyclicks and high
molecular weight material was formed. The yield of cyclics could be adjusted by altering the conditions and catalysts. The mixture of cyclic oligomers, which ranged from \( n = 2 \) to 26 (where \( n \) is the number of repeat units), could be isolated from the high molecular weight material and polymerized to very high molecular weights with low polydispersities. It was also found that the mixture of cyclic oligomers results in a much lower melting point than for the individual isolated oligomers. This allows for ease of processing in the melt to obtain high molecular weight materials.

Various conditions and catalyst systems were systematically investigated.\textsuperscript{32} Research into the mechanism of cyclic formation has resulted in the picture of combined hydrolysis and condensation reactions depicted in Scheme 2.1.2.4.1.\textsuperscript{32}

Research has continued in this area as aromatic macrocyclic carbonates of many different monomers have been synthesized.\textsuperscript{50} This work has also spawned research into the synthesis of macrocyclic oligomers of other classes of polymers including polyarylates,\textsuperscript{29} polyamides, polyimides,\textsuperscript{30,51} poly(arylene ether ketone)s,\textsuperscript{52} and poly(arylene ether sulfone)s.\textsuperscript{53-58}
Scheme 2.1.2.4.1 Tertiary Amine Catalyzed Formation of Cyclics, Linears, and Polymer

2.1.2.5 Other Synthetic Methods

Of the synthetic routes already mentioned, phosgene is currently used at some stage of the reaction. It is either utilized directly in the polycarbonate synthesis, or it is used to make a precursor such as diphenyl carbonate. Phosgene is a highly toxic gaseous material. This has resulted in research
towards identifying ways of circumventing its use in the synthesis of polycarbonates. None of the methods has so far become industrially viable.

Other phosgene derivatives have also been used in the synthesis of polycarbonates by the three major techniques. Some of these will be mentioned here. Although most require the use of phosgene to synthesize the reactant, it may be possible that some phosgene-less route may be found in the future.

Certain diamides such as that obtained from imidazole and phosgene can be used to synthesize polycarbonates by solution processes, but this process has no real benefit. For laboratory reactions, chlorocarboxylic acid trichloromethyl ester (diphosgene) and bis(trichloromethyl)carbonate (triphosgene), can be used instead of phosgene. Since these reactants are solids, they are generally considered to be safer than phosgene. Bis(4-nitrophenyl)carbonate, bis(2-nitrophenyl)carbonate, and other carbonates containing good leaving groups have been investigated as reactants in polycarbonate synthesis. These reactive carbonates can be used either in solution or in low temperature melt reactions under the proper conditions to synthesize high molecular weight polycarbonates.

The melt transesterification with dimethyl carbonate rather than diphenyl carbonate could eliminate the use of phosgene since there are other routes to this compound. Unfortunately this reaction is thermodynamically unfavorable and the dimethyl carbonate degrades at temperatures where the reaction rate is high enough. Patents have been issued for the conversion of dimethyl carbonate to diphenyl carbonate.
Oxidative coupling reactions have been attempted for the synthesis of diaryl carbonates directly from phenols and carbon monoxide,\textsuperscript{3,62,63} as well as by the direct condensation of phenols with carbon dioxide.\textsuperscript{6} Investigations of catalytic processes for the synthesis of polycarbonate directly from the aromatic dihydroxy compound and carbon monoxide have also been performed.\textsuperscript{5} Only low molecular weights were obtained with poor catalyst efficiencies and difficulty of polymer isolation.

2.1.3 Physical Properties

Some of the more important mechanical properties of bisphenol A polycarbonate were listed in Table 1.1. Each of these properties, with the exception of impact strength, has been surpassed by other materials, but the combination of properties is what makes this material so useful.\textsuperscript{64} Many other aromatic polycarbonates and copolycarbonates have been investigated. Schnell references some of the early materials which were studied.\textsuperscript{39} No other polycarbonate has been able to match the combination of properties of bisphenol A polycarbonate, although other polycarbonates and comonomers have found limited use for some applications.

The glass transition temperature (\(T_g\)) for bisphenol A polycarbonate is well known to be about 150°C.\textsuperscript{39} The polymer can crystallize but it is very difficult for this to occur from the melt, and the material is usually obtained in the mostly amorphous form. By annealing at 180°C for 8 days crystallization can be induced.\textsuperscript{5} The crystallization of this material can also be readily induced by a number of solvents.\textsuperscript{65} The melting temperature (\(T_m\)) for this material varies with
the type and amount of crystallinity. Highly crystalline materials (43%) have been reported to melt at approximately 268°C.\textsuperscript{46}

As mentioned several times, bisphenol A polycarbonate is most highly regarded for its exceptional impact strength. The origin of this property has been attributed to low frequency secondary relaxations below $T_g$ which manifest themselves as a broad loss modulus ($G''$) maximum centered at approximately -100°C in the dynamic mechanical spectrum. Bisphenols which contain groups that can hinder rotations cause a shift in this maximum to higher temperatures and also generally result in more brittle materials.\textsuperscript{3} The origin of the secondary relaxations has been widely debated,\textsuperscript{66,67} but has recently been suggested to be the result of segmental motions of up to seven repeat units.\textsuperscript{68}

A ductile to brittle transition occurs below -10°C for bisphenol A polycarbonate.\textsuperscript{69} This transition can be shifted to very low temperatures by the incorporation of polydimethylsiloxane blocks.\textsuperscript{70} The formation of these block copolymers is discussed in section 2.2.4

Bisphenol A polycarbonates are chemically resistant to aqueous acids and bases, although they are hydrolytically cleaved by strong bases.\textsuperscript{5} The material is soluble in a number of chlorinated organic solvents such as methylene chloride, chloroform, 1,1,2,2-tetrachloroethane, and cis-1,2-dichloroethylene, as well as non-halogenated solvents like pyridine and $m$-cresol. While the polymer is insoluble in solvents such as carbon tetrachloride or acetone, these and other solvents promote crystallization of stressed samples.\textsuperscript{5,65} This poor resistance to a number of solvents is the largest drawback to the use of bisphenol A polycarbonate in a number of applications, and a variety of
approaches have been used to circumvent this problem, including the formation of network structures.

2.1.4 Reactive Functional Polycarbonates and the Resulting Crosslinked Networks

Improving the properties of existing polymers has been a major focus of polymer science, and polycarbonates have not been excluded. One method which has been used to alter the properties of thermoplastic materials is to incorporate them into three dimensional networks through the synthesis and subsequent reaction of functional polymers. The formation of such thermosets results in materials with improved solvent resistance and increased dimensional stability, but usually with increased brittleness as well. Since bisphenol A polycarbonate is one of the toughest homopolymers known, its incorporation into a network structure may allow retention of this property. While this idea has been investigated numerous times (utilizing many different reactive groups as shown in Figure 2.1.4.1), very little information has been published outside of the patent literature.
Figure 2.1.4.1 Reactive Moieties Incorporated Into Polycarbonates

Many different reactive groups have been incorporated into aromatic polycarbonates, either along the backbone or more commonly at the chain termini. The types of reactive functionalities of interest are those which yield no byproducts during the crosslinking reaction. The first such reactive polycarbonate was synthesized by the incorporation of 2,2-bis(3-allyl-4-hydroxyphenyl)propane (diallyl bisphenol A) into bisphenol A polycarbonates.\textsuperscript{71,72} This method was investigated further by Kolesnikov et al. in the late 1960's.\textsuperscript{73} Amounts of up to 20 mole percent diallyl bisphenol A were incorporated into the copolymer along with bisphenol A. Films were observed
to partially crosslink when heated above 200°C for 5-10 hours in air, becoming 20-50 percent insoluble in chloroform. Acceleration with azobisisobutyronitrile (AIBN) yielded a completely insoluble network from the 20 mole percent copolymer.

The incorporation of allyl groups at the chain ends has also been reported in the patent literature, where the allyl group was derived from allylphenol, allyl chloroformate, allyl isocyanate, or allyl alcohol.

Cyanate terminated polycarbonates have recently been reinvestigated after first being reported in a 1975 patent. In both references, cyanogen bromide was reacted with phenol terminated polycarbonate oligomers to produce the desired reactive group. Curing above 200°C resulted in reported triazene ring crosslinked networks with high insoluble fractions.

Other typical reactive end groups have been incorporated such as methacrylate, maleimide, and maleimide derivatives such as dimethylmaleimide and dichloromaleimide, with varied results when curing these materials into network structures. In fact, the substituted maleimide terminated polymers remained soluble after thermal treatment, yielding only a slight increase in the solution viscosity.

Benzocyclobutene telechelic oligomers have also recently been synthesized and subsequently thermally cured into insoluble networks. These materials were synthesized predominately for the purpose of better understanding the nature of the crosslinks formed from this reactive group. The polycarbonate network formed from the reactive oligomers was subsequently hydrolyzed by base to obtain bisphenol A and the residual reaction products.
from the crosslinking reaction,\textsuperscript{86} whereby information about the mechanism of benzocyclobutene cure reactions could be elucidated.

Isopropenylphenyl and vinylphenyl groups are the last two reactive terminal groups to be discussed. The incorporation of isopropenylphenyl groups have been studied by the addition of 4- or 3-isopropenylphenol, or derivatives, into a typical interfacial polycarbonate reaction.\textsuperscript{87-89} This end group does not necessarily lead to highly crosslinked species, as soluble block copolymers were reportedly obtained from the reaction with styrene in the presence of dicumyl peroxide.\textsuperscript{90} Vinylphenyl groups on the other hand do lead to highly crosslinked materials.\textsuperscript{91} This end group has been placed at the chain ends of polycarbonates by the introduction of 4-vinylphenol,\textsuperscript{91} or 4-vinylbenzoate\textsuperscript{62} into typical polymerization reactions. The results from the investigation of oligomers obtained from 4-vinylphenol and the resulting networks is presented in this thesis.

The synthesis of polycarbonate networks by the reaction of oligomers with typical thermosetting coreactants has also been investigated. Modified epoxy networks have been synthesized by the reaction of phenol terminated polycarbonate oligomers with diepoxides.\textsuperscript{93,94} Similar materials have also been synthesized by the in situ reaction of epoxides with phenol terminated oligomers produced from the ring opening of cyclic carbonates in the presence of linear polycarbonate.\textsuperscript{95} A side reaction between the aromatic carbonate and the epoxide ring was found to occur in these reactions (Scheme 2.1.4.1).\textsuperscript{94} This side reaction alters the structure of the polycarbonate, yielding a highly crosslinked material containing phenoxy type linkages crosslinked with carbonate units. Due to this reaction, it is impossible to form epoxy terminated
aromatic polycarbonate oligomers by the reaction of excess epoxide with phenol terminated polycarbonates, or well defined networks from them.

\[
\text{Benzyltrimethylammonium chloride} \\
\downarrow \\
\text{Scheme 2.1.4.1 Reaction Between Aromatic Carbonate and Epoxide}
\]

An innovative method of forming crosslinked polycarbonate networks was developed from the recent investigation of cyclic carbonate oligomers. The method consists of ring opening cyclic carbonates in the presence of a bis-cyclic carbonate such as that shown in Figure 2.1.4.2. The ring opening incorporation of this bis-cyclic coreactant results in the formation of crosslinked structures.
2.1.5 Fire Retardant Polycarbonates

2.1.5.1 General Fire Retardants

Imparting fire retardancy to polymeric materials is very important in today's society, as polymers make up a large percentage construction materials. It is very important for buildings and transportation vehicles, where evacuation is difficult, to be resistant to fire, and government legislation is in fact becoming more stringent in this area.

A number of excellent books\textsuperscript{96-99} and reviews\textsuperscript{100,101} on the general subject of fire retardancy of polymers have been written.

Since polycarbonates are used in many applications such as construction, housing, coatings, etc., flame retardancy is a desirable property. Although bisphenol A polycarbonate is considered to be somewhat fire resistant, with an oxygen index of 26 according to ASTM D2863-70 and V2 (1.6 and 3.2 mm) according to UL 94,\textsuperscript{5} safety aspects have led to the search for materials with better fire resistant properties. Flame retardant grades of polycarbonates are available with a variety of additives, comonomers, or blends suitable for improving this property.
Halogen containing polycarbonates, such as those synthesized from tetrabromobisphenol A, are flame retardant. Copolymers with bisphenol A can also be flame retardant and classified VO under UL 94 (3.2 mm thickness), yet the tetrabromobisphenol A is known to decrease the impact toughness of polycarbonate while increasing the T_g.\textsuperscript{5} Other halogenated comonomers such as 2,2-bis(4-hydroxyphenyl)-1,1-dichloroethylene impart good flame retardancy to copolymers.\textsuperscript{5} This particular monomer yields polymers and copolymers which are highly impact resistant; therefore, minimizing the decrease in properties from that of bisphenol A polycarbonate.

The polycarbonate of bis(4-hydroxy-3,5-dimethylphenyl) methane as well as the copolymers with bisphenol A show surprisingly high flame retardancy. The homopolycarbonate is listed V0 (UL 94) at 0.8 mm thickness and has a limiting oxygen index of 43.\textsuperscript{5} Block copolymers of polydimethylsiloxane and polycarbonate also show an improved flame retardancy.\textsuperscript{102}

A large number of additives (too numerous to deal with in this review) have been used for improving the flame retardancy of polycarbonate materials. Some of the more important and more widely used additives consist of saltlike compounds such as C_4F_9SO_3K or sodium trichlorobenzene sulfonate.\textsuperscript{103-105} The mechanism of their flame retardancy is reported to be the formation of crosslinks in the event of a fire.\textsuperscript{5,106}

2.1.5.2 Phosphorus Containing Polycarbonates

Incorporation of phosphorus containing comonomers is another method of improving the fire retardant properties of an existing polycarbonate. Although some phosphorus additives have also been used for this purpose, research has
produced many useful comonomers. The majority of the work in this area has involved the formation of phosphate, or phosphonate linkages in the copolymers by the addition of R-P(X)Cl₂ compounds (such as those demonstrated in Figure 2.1.5.2.1) into polymerization reactions.¹⁰⁷-¹¹² The P—O—C linkages which result from the formation of these copolymers are hydrolytically unstable.

![Diagram of phosphate and phosphonate linkages]

**Figure 2.1.5.2.1** Phosphorus Containing Comonomers Which Form Hydrolytically Unstable P—O—C Bonds

More hydrolytically stable phosphorus containing copolymers have been produced by the synthesis and incorporation of comonomers which do not form backbone P—O—C bonds.¹¹³-¹¹⁷ Examples of these monomers are depicted in Figure 2.1.5.2.2.
Figure 2.1.5.2.2 Phenol and Aliphatic Hydroxyl Functional Phosphorus Monomers

All of the polycarbonates and copolycarbonates derived from these monomers were found to have improved fire resistance properties over bisphenol A polycarbonate.

2.2 Polyorganosiloxanes

The organosiloxanes were first synthesized by Friedel and Crafts in 1863 by the reaction of dialkylzincs with silicon tetrachloride. They worked on the synthesis of organosiloxane compounds through 1880. Ladenburg in 1872 prepared the series of ethylchlorosilanes. He hydrolyzed diethylidichlorosilane to polydiethylsiloxane, but he did not correctly identify the
structure. He assumed the structure to be similar to a ketone and the term silicone was coined.

Kipping and coworkers researched this area of chemistry in the early 1900's and proved the correct polymeric structure, although the term silicones persisted. Today the term siloxanes or polysiloxanes is more accurate, although the silicone terminology persists in the older literature and as a trade name. Kipping is regarded as the founder of siloxane chemistry, publishing 57 papers on the subject covering 45 years of work. During this time, Kipping discovered a more versatile route to organosilanes through the reaction of a Grignard reagent with SiCl₄ and was able to synthesize a great variety of organosilanes. He also synthesized a large number of linear and cyclic organosiloxane polymers through the hydrolysis of functional groups. Kipping was the first to discover the acid and base catalyzed redistribution reactions (which will be discussed in section 2.2.1), but failed to recognize the importance of the polymers as he and his coworkers instead attempted to isolate monomeric crystalline compounds. Kipping also avoided working on what has become the most important organosilanes, the methylsilanes.

Others discovered an interest in the polymeric materials, but the commercialization of these materials was hindered by the lack of a convenient synthesis of monomers. Hyde at Corning Glass Works synthesized polyethylphenylsiloxanes from the hydrolysis of ethylphenylhalosilanes produced by Kipping's Grignard route, and applied this material to the insulation of glass fibers. In the late 1930's, Rochow synthesized methylhalosilanes by Kipping's Grignard route, as well as the corresponding polymers by hydrolysis and condensation, in order to improve upon the
materials synthesized by Hyde.\textsuperscript{121} In 1940 Rochow (and independently Müller shortly thereafter) discovered the direct process for the synthesis of organohalosilanes.\textsuperscript{121} The process involves the high temperature reaction of organic halides with silicon or silicon alloys. Copper catalysts are used for the synthesis of alkylhalosilanes while a silver catalyst is used for the synthesis of phenylhalosilanes. A mixture of products is obtained from this reaction as shown in Scheme 2.1.1. This mixture of organochlorosilane products can be adjusted to maximize the formation of the diorganodichlorosilanes which are the precursors to linear polymers. The products can be fractionally distilled and separated.

\[
\text{RCl} + \text{Si} \xrightarrow{250-300^\circ\text{C}} \xrightarrow{\text{Cu or Ag}} \text{R-Si-Cl} \quad \text{R-Si-Cl} \quad \text{R-Si-Cl} \quad \text{Cl-Si-Cl}
\]

\textbf{Scheme 2.2.1} Direct Synthesis of Organosilanes

As mentioned above, the conditions of the direct synthesis can be adjusted to yield either dimethylidichlorosilane, diphenyldichlorosilanes, or mixed methylphenyldichlorosilanes. These are the most important starting materials for polymer synthesis. Once the monomers are obtained, there are a variety of methods for the synthesis of polymers and oligomers.\textsuperscript{9} These routes include:

1. Hydrolysis of organohalosilanes or derivatives (organoalkoxysilanes, organoacetoxyoxysilanes, etc.),
2. Redistribution or equilibration reactions of cyclic oligomers or low molecular weight linear materials,
3. Non-hydrolytic processes such as the reaction of metal silanlates with organohalosilanes, the reaction of organosilanol with organohalosilanes, the reaction of organosilanol with organo-H-silanes, reaction of organoaminosilanes with
organosilanols, and others which can be found in Noll, \(^9\) (4) Anionic polymerization of the cyclic tetramer with organolithium initiators, and (5) Thermal polymerizations. Only methods (1) and (2) are commercially important.

These monomers can be hydrolyzed directly to polymers, or can be hydrolyzed to form cyclic oligosiloxanes by performing the hydrolysis in the presence of partially water soluble solvents.\(^{122}\) This dilution of the siloxane oligomer allows an intramolecular cyclization to take place preferentially. Controlled hydrolysis can also yield halo-terminated oligomers which can be useful for the polymerization of block copolymers.\(^9\)

2.2.1 Polymerization of Cyclosiloxanes

The cycloorganosiloxanes which can be formed can be polymerized by a ring opening redistribution reaction with either acidic or basic catalysts. The redistribution or equilibration is a result of both linear chains and cyclic oligomers having similar reactivity (except for the strained ring of the cyclic trimer). The Si—O linkages in the polymerization are in this way continuously broken and reformed until an equilibrium state is reached. This equilibrium state is governed by the particular structure, temperature, and solvent conditions of the reaction,\(^6,^{123}\) and is independent of the type of catalyst used.\(^{124,125}\) The equilibrium concentration of cyclics formed in a bulk polymerization decreases in the order: \(^{126,127}\)

\[
\text{H} > \text{CH}_3 > \text{CH}_2\text{CH}_3 > \text{CH}_2\text{CH}_2\text{CH}_3 \sim \text{C}_6\text{H}_5 >> \text{CH}_2\text{CH}_2\text{CF}_3
\]
Dilution of the reaction with an inert solvent leads to an increase in the amount of cyclics at equilibrium.\textsuperscript{123,128}

Endcapped oligomers and polymers can be synthesized by the addition of a variety of endblockers (Scheme 2.2.1.1). These endblockers can contain functional groups resulting in the synthesis of reactive oligomers. Hexaorganodisiloxanes are typical endblockers, although precursors to these disiloxanes such as triorganosilanols, or other monofunctional reactants can also be considered as endblockers. Once the reaction has reached its equilibrium state, the mixture will contain endcapped linear chains (with molecular weight determined by the initial ratio of endblocker to monomer) and low molecular weight cyclics.

\[
\begin{align*}
\text{CH}_3 & \quad \text{CH}_3 \\
R - \text{Si} - \text{O} - \text{Si} - R \\
\text{CH}_3 & \quad \text{CH}_3
\end{align*}
\]

\[
\begin{align*}
\text{CH}_3 & \quad \text{Si} \quad \text{O} \\
\text{Si} & \quad \text{O} \\
\text{Si} & \quad \text{CH}_3 \\
\text{CH}_3 & \quad \text{CH}_3 \\
D_4
\end{align*}
\]

\[
\begin{align*}
\text{Catalyst} & \quad \Delta \\
\uparrow
\end{align*}
\]

\[
\begin{align*}
\text{R} - \left( \begin{array}{c}
\text{Si} \\
\text{CH}_3
\end{array} \right) \quad \text{Si} - R \\
\text{CH}_3 & \quad \text{CH}_3
\end{align*}
\]

\[
\begin{align*}
\text{cyclics}
\end{align*}
\]

\textbf{Scheme 2.2.1.1} Synthesis of Endcapped Polydimethylsiloxane Oligomers by Catalyzed Redistribution
The Si—O bond is considered to be partially ionic. Most authors have quoted the value as being approximately 50% ionic, although more accurate estimates by Hannay and Pauling place the value at closer to 38 - 41%.\textsuperscript{9} Never-the-less, the ionic character of this bond in most cases allows attack by either acids or bases to effect redistribution reactions. Substituents can change the polarity of the bond which can thus affect the susceptibility of the bond to acid attack. For example, hexachlorodisiloxane does not react with Lewis acids such as BF\textsubscript{3}.\textsuperscript{9} In contrast to this situation, substitution by electron donating groups facilitates attack. The choice between acid or base catalysis for redistribution reactions is therefore dictated by the substituents on the organosiloxane, as well as the stability of the functional groups which are to be incorporated.

2.2.1.1 Acid Catalyzed Redistribution

In the acid catalyzed redistribution reaction, many protic and Lewis acids are effective. When a protic acid is used, the first step is the complexation with the siloxane oxygen.\textsuperscript{9} The exact mechanism of the redistribution that follows is not known but is speculated to occur by one of two pathways. In the first, the oxonium complex can decompose to form an Si—OH bond and an Si—X bond from the X\textsuperscript{−} counterion. New siloxane bonds can then be formed by various reforming reactions (Scheme 2.2.1.1.1). The other mechanism has the siloxane oxygen of a non-protonated unit attacking the activated complex (Scheme 2.2.1.1.2), followed by scission and reformation. Lewis acids act similarly by accepting the electron pair from the siloxane oxygen. The most common acids used are sulfuric acids, alkyl and arylsulfonic acids, and trifluoroacetic acid.\textsuperscript{17}
Typical Lewis acid catalysts include iron(III) chloride, aluminum chloride, boron trifluoride, zinc chloride, and tin(IV) chloride.\textsuperscript{9}

\[
\text{Si}^+\text{O}^-\text{Si}^+ + X^- \rightarrow \text{Si-OH} + \text{Si-X}
\]

\[
\text{Si-OH} + X^-\text{Si}^- \rightarrow \text{Si-O-Si}^- + HX
\]

\[
\text{Si-OH} + \text{HO-Si}^- \rightarrow \text{Si-O-Si}^- + H_2O
\]

\[
\text{Si-X} + H_2O \rightarrow \text{Si-OH} + HX
\]

**Scheme 2.2.1.1.1** Possible Decomposition of Onium Complex and Reformation Reactions in Acid Catalyzed Redistribution\textsuperscript{9}

\[
\text{Si}^-\text{O}^-\text{Si}^+ \rightarrow \text{Si}^-\text{O}^-\text{Si}^+ + \text{Si}^-\text{O}^-\text{Si}^- + H^+
\]

**Scheme 2.2.1.1.2** Alternative Acid Catalyzed Polymerization Mechanism\textsuperscript{9}

The acid catalysis is used less often than the corresponding base catalyzed reaction, but is especially important for the polymerization of organosiloxanes with Si–H functionality, as the Si–H functionality cannot survive the exposure to alkaline catalysts.\textsuperscript{9} Acid catalysis is also important for the equilibration with organohalosiloxanes to synthesize halogen terminated oligomers via catalysis with iron(III) chloride hexahydrate.\textsuperscript{9,129}

2.2.1.2 Base Catalyzed Redistribution
A variety of basic compounds can be used to polymerize cyclic organosiloxanes including alkali metal hydroxides, alkali metal alkoxides, quaternary ammonium and phosphonium hydroxides, and the silanolates derived from these bases.\textsuperscript{9} The catalysts must be removed from the product to ensure stability. This is often carried out by washing or neutralization steps. The quaternary ammonium and phosphonium hydroxides and silanolates are considered transient catalysts since they can be removed from the reaction by decomposition at elevated temperature.\textsuperscript{130} They degrade between 110 and 150°C to yield volatile by-products which can be easily removed from the system.

The basic catalysis involves the attack of the base on the electropositive silicon atom,\textsuperscript{125,131} while the subsequent reaction steps can be written as for the acid catalyzed reaction (Scheme 2.1.1.2.1).

\[
\begin{align*}
\text{Si-O-Si}^- & + \text{KOH} \rightarrow \text{Si-O-Si}^- + \text{K}^+ \\
\text{Si-O-Si}^- & \rightarrow \text{Si-O}^- + \text{HO-Si}^- \\
\text{Si-O-Si}^- & + \text{KOH} \\
\end{align*}
\]

Scheme 2.2.1.2.1 Mechanism of Base Catalyzed Equilibration\textsuperscript{9}

The equilibration of octamethylcyclotetrasiloxane in the presence of hexamethyldisiloxane endblockers results in a viscosity profile such that the viscosity initially increases greatly and then equilibrates to its final value.\textsuperscript{125} The reactivity of the the cyclic tetramer is greater than that of the disiloxane causing an initial increase in viscosity and molecular weight before
equilibration occurs. The kinetics of the base catalyzed redistribution relative to different catalysts have been studied for specific systems.

2.2.3 Functional Organosiloxanes

There are two basically different types of functionalized polyorganosiloxanes: those that contain a functional group directly attached to Si, and those that contain a functional group attached to Si through a short chain hydrocarbon.

Organosiloxane oligomers with Si—X functionality are known for a variety of X groups (Table 2.2.3.1).

Table 2.2.3.1 General Structure of Si—X Functional Organosiloxane Oligomers

\[
\begin{align*}
X & = \text{—Cl, —OH, —OCH}_3, \quad \text{—OC}_2\text{H}_5, \\
& \quad \text{—H, —NH}_2, \quad \text{—N(CH}_3)_2, \quad \text{—CH=CH}_2. \\
 n & = \text{Number of repeating units} \\
 R & = \text{An organic radical, usually —CH}_3
\end{align*}
\]
The chloro functional siloxanes can be obtained through the controlled hydrolysis of dichlorosilanes or through the ferric chloride hexahydrate catalyzed redistribution in the presence of dichlorosilanes. Once obtained, these oligomers can be reacted with a variety of nucleophiles to obtain other functional oligomers or to form copolymers directly. Most of these functional groups are reacted with phenols to form Si—O—C bonds.

The formation of Si—O—C bonds can be undesirable due to hydrolytic instability. It is well known that Si—O—C bonds are often used as protecting groups for the OH functionality and that the regeneration of the OH functionality through hydrolysis is a facile reaction. This site is therefore a potentially hydrolytically unstable linkage. The hydrolytic stability of copolymers containing this linkage is often greater than would be expected. The hydrophobic nature of both the organosiloxane and the organic polymer blocks exclude water well enough to yield good hydrolytic stability.

The Si—H functional oligomers can be obtained by the acid catalyzed equilibration reaction using tetramethyldisiloxane as an endblocker. These are very useful for subsequent hydrosilation reactions. The Si—H functional tetramethyldisiloxanes are used to synthesize a majority of functional siloxanes without the formation of hydrolytically unstable bonds.

Many siloxane oligomers with Si—R—X functionality have been synthesized and incorporated into copolymers. The copolymers obtained from organosiloxane oligomers with Si—R—X functionality are usually more hydrolytically stable than the corresponding copolymers obtained from oligomers with Si—X functionality. The synthesis of these oligomers relies on the ability to synthesize functional disiloxanes or disiloxane precursors.
Functional disiloxanes are the key reactants in forming α,ω-organofunctional oligomers. These disiloxanes can be synthesized by a variety of methods, but the most preferred method is that of hydrosilation between a functional olefin and the Si—H. The starting material is usually either tetramethyldisiloxane or chlorodimethyldisiloxane and an olefinic compound with the desired functionality.\textsuperscript{17} Allylic compounds tend to work well in these reactions and are the most often used.\textsuperscript{11} The most often used catalyst for this reaction is chloroplatinic acid (H\textsubscript{2}PtCl\textsubscript{6} • 6H\textsubscript{2}O), although a variety of Pt derivatives are effective and can have certain advantages in some systems. Other methods of synthesizing disiloxanes usually involve organometallic compounds such as Grignard reagents, organolithium compounds, etc.\textsuperscript{135}

2.2.4 Polycarbonate-Polydimethylsiloxane Copolymers

There are many different types of functional siloxane oligomers, useful as endblockers, that can be found in the literature. Many of these are reviewed in Noll,\textsuperscript{9} and in ref.\textsuperscript{17} These can be incorporated as blocks into a variety of different copolymers.\textsuperscript{17,136,137} What will be reviewed here will be those useful for the synthesis of polycarbonate copolymers. This will include phenol, aliphatic hydroxyl, carboxylic acid, silylchloride, and silylamine end groups, as well as others.

Copolymers of polydimethylsiloxanes and polycarbonates were first synthesized by Vaughn in 1965.\textsuperscript{138} The method utilized for the synthesis of the copolymers is shown in Scheme 2.2.4.1.\textsuperscript{137,139} The α,ω-dichloro-terminated polydimethylsiloxane oligomers can be synthesized by the acid catalyzed redistribution reaction of D\textsubscript{4} in the presence of dichlorodimethylsilane.\textsuperscript{9,129}
Copolymers were formed in situ by first reacting the chloro-terminated oligomers with an excess of bisphenol A in the presence of pyridine followed by phosgenation of the mixture.

\[
\text{D}_4 + \text{Cl-Si-Cl} \xrightarrow{\text{FeCl}_3 \cdot 6\text{H}_2\text{O}} \text{Cl-Si-O-Si-O-Si-O-Si} + \text{cyclics}
\]

\[
\text{Cl-Si-O-Si-Cl} + \text{BPA} \xrightarrow{\text{pyridine} \cdot \text{CH}_2\text{Cl}_2} \text{HO-BPA-O-Si-O-BPA-OH}
\]

**Scheme 2.2.4.1 Synthesis of Polydimethylsiloxane-Polycarbonate Copolymers From Bisphenol A Terminated Polydimethylsiloxanes**

The reaction conditions create a wide range of block size distribution within the copolymers. Since the carbonate blocks are formed *in situ*, siloxane blocks can be coupled together. Furthermore, the possibility exists for the formation of coupled siloxane blocks through the reaction with bisphenol A in the first step.
Williams and coworkers developed $^{13}$C and $^{29}$Si NMR techniques to address this problem. They were able to determine the number of isolated bisphenol A groups in the copolymer as well as the number average molecular weights of each block. Work by Niznik and Legrand attempted to determine the extent of coupling of the siloxane oligomers in the first step by comparing GPC curves before and after reaction with bisphenol A. They found good correlation with what would be expected from stoichiometry. The coupling of the oligomers by phosgene in the subsequent step was not addressed.

These materials and this method of copolymerization have been the most widely studied of polydimethylsiloxane-polycarbonate copolymers and can be found in references, as well as numerous other journal articles and patents.

In all cases, two phases were found to exist in the copolymers. This has been attributed to the large differences in the solubility parameters of the two components ($\delta$ polycarbonate = 10 (cal/cm$^3$)$^{1/2}$ and $\delta$ polydimethylsiloxane = 7.5 (cal/cm$^3$)$^{1/2}$). Two glass transition temperatures are also found to exist, related to the two components. The glass transition temperatures of the copolymers were found to correspond very well with those that would be expected for the homopolymers with molecular weights similar to those in the block segments. Deviation from the Tg's expected for the polycarbonate oligomers (assuming perfect alternation of blocks) was found only to be significant at very low block sizes of the dimethylsiloxane oligomers, indicating that only a small amount of polydimethylsiloxane is present in the polycarbonate phase.
Other workers addressed the phase separation in these systems, using a different more controlled approach.\textsuperscript{13,40,152} Perfectly alternating copolymers of polydimethylsiloxane and polycarbonate were synthesized by a different route. Dimethylamino-terminated dimethylsiloxane oligomers were synthesized, and were reacted with preformed phenol-terminated polycarbonate oligomers to synthesize perfectly alternating copolymers as shown in Scheme 2.2.4.2. A series of copolymers were synthesized where the compositions remained constant at approximately 50 weight percent of each component while varying the block lengths of each component.\textsuperscript{152} It was found that the possible content of polydimethylsiloxane in the polycarbonate phase ranged from 1.3\% for large block sizes to approximately 11\% for the small block sizes as shown in Table 2.2.4.1.\textsuperscript{152}

\begin{align*}
\text{N-Si-O-Si-N} & \quad + \quad \text{Si-O-Si} \quad \xrightarrow{\text{Tetramethylammonium hydroxide}} \quad \text{cyclics} + \quad \text{N-Si-O-Si-N} \\
\text{H-[O-} & \quad \text{H} \quad \xrightarrow{\text{Chlorobenzene}} \quad \text{130\textdegree C}} \quad \text{Perfectly Alternating Copolymer with Si-O-C Bonds}
\end{align*}

**Scheme 2.2.4.2** Synthesis of Copolymers From Silylamine Terminated Dimethylsiloxane Oligomers and Phenol Terminated Polycarbonate Oligomers
Table 2.2.4.1 Amount of Phase Mixing From Tg Data

<table>
<thead>
<tr>
<th>&lt;M&lt;sub&gt;n&lt;/sub&gt;&gt; of PC block, (kg/mole)</th>
<th>T&lt;sub&gt;g&lt;/sub&gt; of pure PC (DTA) (°C)</th>
<th>PC T&lt;sub&gt;g&lt;/sub&gt; in copolymer (Rheovlbron) (°C)</th>
<th>PC T&lt;sub&gt;g&lt;/sub&gt; in copolymer (DSC) (°C)</th>
<th>Weight % of PDMS in PC domains (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>16.0</td>
<td>149</td>
<td>155</td>
<td>139</td>
<td>1.34</td>
</tr>
<tr>
<td>11.5</td>
<td>145</td>
<td>148</td>
<td>132</td>
<td>1.80</td>
</tr>
<tr>
<td>4.2</td>
<td>131</td>
<td>125</td>
<td>108</td>
<td>3.56</td>
</tr>
<tr>
<td>3.4</td>
<td>125</td>
<td>110</td>
<td>98</td>
<td>4.40</td>
</tr>
<tr>
<td>3.1</td>
<td>123</td>
<td>108</td>
<td>91</td>
<td>5.36</td>
</tr>
<tr>
<td>1.8</td>
<td>101</td>
<td>60</td>
<td>48</td>
<td>11.06</td>
</tr>
</tbody>
</table>

This synthetic method allowed for the synthesis of well defined blocks, but Si—O—C bonds between the blocks remained. Another approach was used to replace this linkage with the more hydrolytically stable Si—C bond between blocks. Hydroxybutyl and hydroxypropyl-terminated oligomers were synthesized and reacted with bisphenol A bischloroformate in pyridine/methylene chloride to form functional oligomers. The oligomers were then reacted with more bisphenol A under interfacial conditions to synthesize in situ copolymers. The problems with this type of reaction is the difference in reactivity of the aliphatic hydroxyl groups versus aromatic hydroxyl groups. The use of aliphatic hydroxyl-terminated polydimethylsiloxanes with different
aliphatic or aliphatic ether spacer groups has been studied repeatedly.\textsuperscript{153-158} The chloroformates of these hydroxyl terminated oligomers are formed and then reacted with bisphenol A by either solution or interfacial processes. The thermal stability of the copolymers depends greatly on the length and type of spacer group.\textsuperscript{157} The copolymers derived from the hydroxymethyl-terminated siloxanes degraded relatively quickly at temperatures above 220°C while copolymers derived from hydroxyethyleneoxymethyl terminated siloxanes were much more thermally stable.

Other routes to siloxane carbonate copolymers can be found in the literature resulting in either Si—O—C bonds or Si—C bonds depending on the procedure. These routes will be presented with the ones that yield Si—O—C bonds first.

Phenol terminated polycarbonates have been reacted directly with siloxane oligomers with Si—Cl functionality.\textsuperscript{159} This process was one of the first methods used for the synthesis of these copolymers, but has recently been reinvestigated.\textsuperscript{160,161} The innovation of the recent research is in the method of forming the phenol terminated polycarbonate oligomers. The oligomers were obtained by the ring opening polymerization of cyclic oligocarbonates in the presence of bisphenol A. The sequential ring opening of cyclic carbonates and D₄ has also been used to form copolymers.

Similar copolymers could be formed through the reaction of phenol terminated polycarbonates with alkoxy-terminated siloxane oligomers.\textsuperscript{162} Si—O—C bonds are also formed in the reaction of an excess of bisphenol (bisphenol A or 4,4'-dihydroxybenzophenone) with acetoxy terminated siloxane oligomers.\textsuperscript{163-165} These phenol functional oligomers were reacted with
bisphenols by solution and interfacial techniques to form in situ copolymers similar to those originally produced by Vaughn.\textsuperscript{138}

Although copolymers containing Si—O—C bonds were the first to be synthesized and are the simplest and most economical of this type of copolymer, much research has gone into the synthesis of the properly functionalized siloxane oligomers which would eliminate this linkage. Many different approaches have been used and will be reviewed.

The first method, which formed polyester linkages between block segments, involved the reaction between carboxylpropyl-terminated polysiloxane oligomers with bishenol A and phosgene under phase transfer catalyzed interfacial conditions.\textsuperscript{13,166} A pre-phosgenation step in the absence of water was used to convert the carboxypropyl-terminated polydimethylsiloxane oligomers into the acid chloride form before reaction with bisphenol A and phosgene under interfacial conditions. No anhydride links could be detected under the conditions used.

Another method by which Si—C bonds are formed and phenol functionality is obtained is through the reaction of an unsaturated phenol with Si—H functional polysiloxane oligomers. This reaction has been researched by a number of different groups using predominately allylphenol derivatives.\textsuperscript{167-170} The 3-(2-hydroxyphenyl)propyl-terminated siloxane oligomers which can be obtained are then reacted with bisphenol A (or its chloroformate) and phosgene by solution or interfacial techniques to derive the in situ produced copolymers. Other unsaturated compounds have also been used such as 4-acetoxy styrene.\textsuperscript{171,172} The acetoxy protecting group can easily be cleaved under the reaction conditions to obtain a phenol functional siloxane.
Triblock copolymers could also be synthesized by a variation of this
method.\textsuperscript{171} $\alpha$-Hydro-$\omega$-methyldimethylosiloxane oligomers were prepared by the
ring-opening polymerization of D$_3$ with LiSiMe$_3$ followed by termination with
dimethylchlorosilane. The monofunctional siloxane could then be reacted with
4-acetoxy styrene to form a monophenol-terminated polydimethylsiloxane
oligomer. Cleavage of the acetoxy group and subsequent polymerization with
bisphenol A and phosgene led to the formation of the desired triblock materials.
Alternatively the same polydimethylsiloxane oligomer could be reacted with
diallylbisphenol A or a polycarbonate containing diallylbisphenol A to
synthesize graft copolymers.\textsuperscript{172}

The formation of functional oligomers with direct Si—aryl bonds has also
been researched. This is also the direction which our research has taken. The
first reference to this type of functionalization can be found in the work of Moehs
and Davidson.\textsuperscript{173} They reacted the diliithium anion of bromophenol with 1,3-
dichlorotetramethyldisiloxane to form the siloxanylene linked bisphenol. They
did not attempt to use this oligomer for polymerizations.

A different approach to synthesize similar bis(hydroxyphenyl)tetramethyl-
disiloxanes was patented by Mironov et al.\textsuperscript{174} They obtained the disiloxane by
forming the Grignard reagent of dimethylsilyl protected bromophenols.
Rearrangement at elevated temperatures resulted in the formation of
dimethylsilyl substituted phenols which could be hydrolyzed to the silanol and
subsequently coupled to the disiloxane. Although it was suggested that
polymers could be formed from these monomers, no polymerizations were
mentioned.
Rosenberg et al. also synthesized a number of bis(hydroxyaryl)tetramethyl-disiloxanes.\textsuperscript{175,176} These workers formed the Grignard reagent from benzyl ether protected bromophenols which were then reacted with chlorodimethylsilane. The resulting silane was then hydrolyzed to the silanol and coupled to form the disiloxane or reacted with bis(dimethylamino)dimethylsilane to form the hexamethyltrisiloxane. Pure bisphenols could not be synthesized by these methods and subsequent polymerizations did not yield high molecular weight materials. Carbonate linked siloxanylenes could be synthesized by a variation of this approach. Dimethylsilylphenol was prepared and reacted with phosgene. The resulting bis(dimethylsilylphenyl)carbonate was oxidized to the bis(silanol). Polymerization by coupling the silanols was found to take place when phosgene was introduced in the presence of pyridine. A number of different carbonate containing polysiloxanylenes were prepared by this method, but each contained only one carbonate group per repeat unit.

Pure phenol functionalized disiloxanes have been synthesized.\textsuperscript{177} The Grignard reagent of tetrahydropyran protected p-bromophenol can be reacted with dichlorodimethylsilane. The resulting chlorosilane can be hydrolyzed and deprotected to form the phenol functional disiloxane. The disiloxanes have been coupled with diacid chlorides to synthesize polyesters of high molecular weight.\textsuperscript{178}

Others have synthesized phenol functional dimethylsiloxane oligomers by the multistep procedure outlined in Scheme 2.2.4.3.\textsuperscript{179} These oligomers were incorporated into polycarbonates by interfacial and solution techniques. The interfacially produced copolymers were reported to be thermally unstable.
Scheme 2.2.4.3  Synthesis of Hydroxyphenylimide Functional Dimethylsiloxane Oligomers
Aromatic carboxylic acid functional disiloxanes such as 1,3-bis(p-carboxyphenyl)tetramethyldisiloxane can also be synthesized by the mild oxidation of 1,3-bis(p-tolyl)tetramethyldisiloxane.$^{180}$ This has recently been incorporated into polycarbonates resulting in aromatic ester linkages between blocks.$^{38,181}$
3.0 EXPERIMENTAL

3.1 General Solvents and Reagents

The following solvents were used as received from Fisher Scientific: methylene chloride (HPLC grade), chloroform, methanol, ethanol, acetone, anhydrous diethyl ether, hexanes, ethyl acetate, toluene, and 1,1,2,2-tetrachloroethane.

The following general reagents were obtained from Aldrich Chemical and used as received: magnesium turnings, potassium t-butoxide (95%), p-toluene-sulfonic acid monohydrate, benzophenone, sodium, and tetraethylammonium bromide.

The following reagents were obtained from Fisher Scientific and used as received: sodium hydroxide, potassium hydroxide (85%), and calcium hydride.

3.2 Purification of Solvents

3.2.1 Tetrahydrofuran (THF)

Chemical Structure:

![Chemical Structure Image]

Source: Fisher Scientific
Empirical Formula: C₄H₈O
Molecular Weight, g/mol: 72.10
Boiling Point, °C/mm Hg: 67/760
Density, g/ml: 0.866

Purification Procedure:

THF was purged with argon and then refluxed under argon in the presence of sodium metal and a small amount of benzophenone. Once the purple color
of the sodium benzophenone ketyl was observed, the THF was distilled as needed into flame dried round bottom flasks and sealed with rubber septa.

3.2.2 Triethylamine (TEA)

Chemical Structure:

\[
\begin{array}{c}
\text{N} \\
\text{CH}_2\text{CH}_3 \\
\text{CH}_3 \\
\text{CH}_2\text{CH}_3
\end{array}
\]

Source: Aldrich

Empirical Formula: C\(_6\)H\(_{15}\)N

Molecular Weight, g/mol: 101.19

Boiling Point, °C/mm Hg: 89-90/760

Density, g/ml: 0.726

Purification Procedure:

Triethylamine was refluxed over pulverized calcium hydride for 24 hours. A distillation apparatus was attached, and the dried TEA was then distilled under argon and stored over molecular sieves.

3.2.3 Pyridine

Chemical Structure:

\[
\begin{array}{c}
\text{N}
\end{array}
\]

Source: Aldrich Chemical

Empirical Formula: C\(_5\)H\(_5\)N

Molecular Weight, g/mol: 79.10

Boiling Point, °C/mm Hg: 114-115/760

Density, g/ml: 0.979
Purification Procedure:

The purification procedure was the same as that for triethylamine (3.2.2).

3.2.4 Chlorobenzene

Chemical Structure:

\[
\text{\begin{tikzpicture}
\node[above] at (0,0) {Cl};
\end{tikzpicture}}
\]

Source: Fisher Scientific

Empirical Formula: \( \text{C}_6\text{H}_5\text{Cl} \)

Molecular Weight, g/mol: 112.56

Boiling Point, °C/mm Hg: 132/760

Density, g/ml: 1.107

Purification Procedure:

Chlorobenzene was purified by refluxing over calcium hydride for 24 hours. It was then distilled into a round bottom flask, after discarding the first 25 ml. The flask was sealed with a rubber septum and purged with argon.

3.3 Preparation and Purification of Monomers and Reagents

3.3.1 2,2-Bis(4-hydroxyphenyl)propane (Bisphenol A)

Chemical Structure:

\[
\text{\begin{tikzpicture}
\node[above] at (0,0) {OH};
\end{tikzpicture}}
\]

Source: Dow Chemical Company

Empirical Formula: \( \text{C}_{15}\text{H}_{16}\text{O}_2 \)

Molecular Weight, g/mol: 228.29

Melting Point, °C: 156-157

Purification Procedure:
Bisphenol A was received as monomer grade Dow Parabis and used without further purification.

3.3.2 4-t-Butylphenol

Chemical Structure:

\[ \text{Chemical Structure} \]

Source: Aldrich
Empirical Formula: C_{10}H_{14}O
Molecular Weight, g/mol: 150.22
Melting Point, °C: 98-101

Purification Procedure:

4-t-Butylphenol was used as received (99+%).

3.3.3 Phosgene

Chemical Structure:

\[ \text{Chemical Structure} \]

Source: Matheson
Empirical Formula: CCl_{2}O
Molecular Weight, g/mol: 98.91
Boiling Point, °C/mmHg: 7.6/760

Purification Procedure:

Phosgene was obtained in 1 or 5 lb cylinders from Matheson. The reagent was dispensed from the cylinder as a gas. The amount dispensed was measured by monitoring the gas flow through a calibrated teflon flow meter.
3.3.4 3,4-Dihydro-2H-pyran

Chemical Structure:

\[ \text{\textbf{Chemical Structure}} \]

Source: Aldrich
Empirical Formula: C₅H₈O
Molecular Weight, g/mol: 84.12
Boiling Point, °C/mmHg: 86/760

Purification Procedure:

3,4-Dihydro-2H-pyran was used as received (97%).

3.3.5 4-Hydroxybenzaldehyde

Chemical Structure:

\[ \text{\textbf{Chemical Structure}} \]

Source: Aldrich
Empirical Formula: C₇H₆O₂
Molecular Weight, g/mol: 122.12
Melting Point, °C: 117-119

Purification Procedure:

100g of 4-hydroxybenzaldehyde was recrystallized from 290 ml of toluene
and dried at 50°C for 24 hours at 1mm Hg.
3.3.6 Methyltriphenylphosphonium bromide

Chemical Structure:

![Chemical Structure](image)

Source: Aldrich
Empirical Formula: C_{19}H_{18}BrP
Molecular Weight, g/mol: 357.24
Melting Point, °C: 230-234

Purification Procedure:

Methyltriphenylphosphonium bromide was used as received (98%).

3.3.7 4-Bromophenol

Chemical Structure:

![Chemical Structure](image)

Source: Aldrich
Empirical Formula: C_{6}H_{5}BrO
Molecular Weight, g/mol: 173.01
Melting Point, °C: 64-68

Purification Procedure:

p-Bromophenol (200g) was recrystallized from 600 ml of a 10:1 mixture of hexanes and toluene. A seed crystal was required to keep the material from separating as an oil. The crystals (platelets) obtained by slow cooling were
filtered, washed with cold hexanes, and dried at room temperature under a reduced pressure of 1mm Hg.

3.3.8 2-(4-Bromophenoxy)tetrahydropyran

Chemical Structure:

\[
\text{Br} - \begin{array}{c}
\text{O} \\
\text{O}
\end{array} - \text{C}_6\text{H}_4
\]

Source: Synthesized
Empirical Formula: C\text{\textsubscript{11}}H\text{\textsubscript{13}}Br\text{\textsubscript{O2}}
Molecular Weight, g/mol: 257.13
Melting Point, °C: 55-56

Synthesis Procedure:

The procedure was a modification of the procedure in ref.\textsuperscript{182} 100g (0.578 mol) of 4-bromophenol was dissolved in 44.52g (0.529 mol) of 3,4-dihydro-2H-pyran in a 500 ml round bottom flask which was cooled with an external ice bath. An addition funnel was attached, and 46.19g (0.549 mol) of 3,4-dihydro-2H-pyran containing 3 drops concentrated HCl was added dropwise over 30 minutes. After complete addition, the mixture was stirred for 2 hours at which time 400 ml of ether was added. The solution was washed 3 times with 2.5M NaOH to remove any unreacted 4-bromophenol, followed by 3 times with water. The organic layer was dried over magnesium sulfate, filtered, and the solvent removed by rotary evaporation to yield 142.88g (96%) of 2-(4-bromophenoxy)tetrahydropyran. The white crystals were recrystallized from 280 ml of 95% ethanol to obtain 131.45g (92%).
3.3.9 4-(4-Bromophenyl)phenol

Chemical Structure:

Source: Aldrich
Empirical Formula: C₁₂H₉BrO
Molecular Weight, g/mol: 249.11
Melting Point, °C: 164-166

Purification Procedure:

4-(4-Bromophenyl)phenol (97%) was used as received.

3.3.10 2-(4-(4-Bromophenyl)phenoxy)tetrahydropyran

Chemical Structure:

Source: Synthesized
Empirical Formula: C₁₇H₁₇BrO₂
Molecular Weight, g/mol: 333.23
Melting Point, °C: 116-117

Synthesis Procedure:

30.00g (0.120 mol) of 4-(4-bromophenyl)phenol, 10.13g (0.120 mol) 3,4-dihydro-2H-pyran, and 30 ml of ether were charged to a 250ml round bottom flask equipped with a magnetic stir bar. An addition funnel was attached and 10.13g (0.120 mol) 3,4-dihydro-2H-pyran containing 3 drops concentrated HCl was added dropwise over 20 minutes while cooling with an ice bath. The mixture continued to stir for 15 hours after which the precipitated product was
removed by filtration, washed with ether, and dried under vacuum at room
temperature to yield 31.05g (78%) 2-(4-(4-
bromophenyl)phenoxy)tetrahydropryan. Elemental analysis calculated for
C_{17}H_{17}BrO_{2}: C, 61.28; H, 5.14. Found: C, 61.37; H, 5.16.

3.3.11 Octamethycyclotetrasiloxane (D₄)

Chemical Structure:

![Chemical Structure Image]

Source: General Electric Company
Empirical Formula: C₈H₂₄O₄Si₄
Molecular Weight, g/mol: 296.62
Density, g/ml: 0.956
Boiling Point, °C/mm Hg: 175-176/760

Purification Procedure:

Octamethylcyclotetrasiloxane (D₄) was refluxed over pulverized calcium
hydride for 24 hours. A distillation apparatus was attached, and the D₄ was
distilled into a round bottom flask and sealed with a rubber septum until
needed.

3.3.12 Dichlorodimethylsilane

Chemical Structure:

```
  Cl-Si-Cl
```

64
Dichlorodimethylsilane was distilled under argon immediately prior to use.

3.3.13 Dimethyl-4-(tetrahydropyranyl-2-oxy)phenylsilanol
(THP-P-Silanol)

Chemical Structure:

\[
\begin{align*}
\text{Source:} & \quad \text{Synthesized} \\
\text{Empirical Formula:} & \quad \text{C}_{13}\text{H}_{20}\text{O}_{3}\text{Si} \\
\text{Molecular Weight, g/mol:} & \quad 252.39 \\
\text{Melting Point, °C:} & \quad 54-55 \\
\end{align*}
\]

Synthesis Procedure:

The following is a modification of the procedure of Matsukawa.\textsuperscript{177} Magnesium turnings (5.20 g; 0.214 mol), a magnetic stir bar, and a crystal of iodine were placed in a flame dried, 3 neck, 500 ml round bottom flask equipped with a mechanical stirrer, condenser, and addition funnel. The contents were further flame dried under argon purge. The flask was sealed with rubber septa while a positive argon pressure was maintained. A solution of 2-(4-bromophenoxy)tetrahydropyran (50.02 g; 0.194 mol) in 100 ml THF was introduced to the addition funnel via cannula and added dropwise over 3 hours to the magnesium suspension while cooling the reaction flask with a cold water
bath. Into a second flame dried, 2 neck, 500 ml reaction flask equipped with an addition funnel was added dichlorodimethylsilane (23.60 ml; 0.194 mol) and 50 ml THF. The Grignard reagent was transferred into the addition funnel via cannula and added to the dichlorodimethylsilane solution dropwise over 2-3 hours while cooling with an ice bath. The reaction mixture was allowed to warm to room temperature and stirred for 12 hours. The contents of the flask were then transferred by cannula to a mechanically stirred mixture of 200 ml 1M aqueous NaHCO₃ and 100 ml ether. The organic layer was separated and washed 4 times with water. The ether was removed by rotary evaporation to obtain a slightly yellow oil which was crystallized from hexanes to yield 34.42g (70%) of white crystals. Elemental analysis calculated for C₁₃H₂₀O₃Si: C, 61.87; H, 7.99. Found: C, 61.72; H, 8.01.

3.3.14 4-(4-(Tetrahydropranyl-2-oxy)phenyl)phenyldimethylsilanol (THP-BP-Silanol)

Chemical Structure:

![Chemical Structure]

Source: Synthesized

Empirical Formula: C₁₉H₂₄O₃Si

Molecular Weight, g/mol: 328.48

Melting Point, °C: 101.5-102.5

Synthesis Procedure:

The synthesis was similar to that of dimethyl-4-(tetrahydropranyl-2-oxy)phenylsilanol (3.3.13). A solution of 2-(4-(4-bromophenyl)phenoxy)-tetrahydropyran (20.00g; 60.0 mmol) in 80 ml THF was added dropwise over 3
hours from an addition funnel to a suspension of iodine etched magnesium turnings (1.61g; 66.0 mmol) and 5 ml THF in a flame dried, 3 neck round bottom flask under argon. The reaction was cooled with an external water bath. The Grignard reagent obtained was transferred via cannula to an addition funnel attached to a rubber septa sealed 2 neck round bottom flask containing a solution of dichlorodimethylsilane (7.30 ml; 60.0 mmol) in 25 ml THF. The Grignard reagent was added dropwise over 2-3 hours under argon while cooling with an ice bath. The reaction mixture stirred at room temperature for an additional 12 hours before being transferred by cannula to a flask containing a stirred mixture of 100 ml 1M NaHCO₃ and 80 ml ether. The mixture was extracted with ether and washed 4 times with water. The ether was stripped by rotary evaporation and the resulting yellow crystals were recrystallized from ether to yield 10.65g (54%) of white crystals. Elemental analysis calculated for C₁₃H₂₀O₃Si: C, 69.47; H, 7.37. Found: C, 69.39; H, 7.39.

3.3.15 4-Acetoxy styrene

Chemical Structure:

![Chemical Structure](image)

Source: Received from Höechst-Celanese and also Synthesized

Empirical Formula: C₁₀H₁₀O₂

Molecular Weight, g/mol: 162.19

Melting Point, °C: 7-8

Boiling Point, °C/mm Hg: 67/0.3

Purification Procedure:
4-Acetoxystyrene was received from Höechst-Celanese in 96% purity. The impurity was 4-acetoxyethylbenzene. Purification by distillation at reduced pressure using a spinning band distillation apparatus could not remove the impurity. The commercial material was dried over calcium hydride for 3 days and distilled through a short path distillation apparatus.

Synthesis Procedure:

Alternatively, pure 4-acetoxystyrene was synthesized by the following procedure: Methyltriphenylphosphonium bromide (198.30g; 0.56 mol) was added to an oven dried, 3 neck, 2000 ml round bottom flask equipped with a mechanical stirrer and condenser. The flask was flame dried under argon purge. Potassium t-butoxide (112.22g; 1.00 mol) was added and 750 ml THF was transferred via cannula while cooling with an ice bath. A dry addition funnel containing 4-hydroxybenzaldehyde (45.18g; 0.37 mol) was attached and the solid was dissolved in 150 ml THF. The solution was added dropwise to the yellow ylide solution while the resulting exotherm was controlled by the ice bath. The reaction mixture stirred for 36 hours under positive argon pressure. The reaction was stopped by the addition of 100 ml water. 400 ml of ether were added and the product was extracted with water. The combined water extracts were back extracted with methylene chloride to yield a yellow aqueous layer. The aqueous layer contained the potassium phenolate of 4-hydroxystyrene. This was placed in a 1000 ml Erlenmeyer flask and acetic anhydride (141 ml; 1.50 mol) was added while stirring with a magnetic stir bar. The organic layer quickly separated. After 1 hour, the product was extracted with ether and washed with water. The ether was removed by rotary evaporation, and the orange oil was distilled under reduced pressure (67°C/0.3 mm Hg) leaving
behind 10 ml of dark liquid. The colorless product was redistilled from 0.5g phenothiazene to yield 45.06g (75% yield) of colorless oil which crystallized upon storage at -10°C.

3.3.16 Bis(4-vinylyphenyl) carbonate

Chemical Structure:

\[
\begin{array}{c}
\text{\includegraphics[width=0.2\textwidth]{chemical_structure}}
\end{array}
\]

Source: Synthesized
Empirical Formula: C\(_{17}\)H\(_{14}\)O\(_3\)
Molecular Weight, g/mol: 266.30
Melting Point, °C: 87.5-88.5

Synthesis Procedure:

An aqueous solution of the potassium phenolate of 4-hydroxystyrene was prepared and isolated as in section 3.3.15 from 4-hydroxybenzaldehyde (15.00g; 0.123 mol), methytriphenylphosphonium bromide (64.50g; 0.181 mol), and potassium t-butoxide (43.0g; 0.38 mol). The aqueous solution was subjected to interfacial phosgenation in 100 ml of methylene chloride with triethylamine (2.74 ml; 0.02 mol) as catalyst. Phosgene was added until the pH dropped to 9.5. The methylene chloride layer was separated, washed twice with 0.5 M HCl, and four times with water. The methylene chloride was then stripped by rotary evaporation and the resulting slightly yellow crystals were recrystallized from 80 ml of 90% ethanol to yield 11.78g (72% yield) of white crystals. Elemental analysis calculated for C\(_{17}\)H\(_{14}\)O\(_3\): C, 76.68; H, 5.30. Found: C, 75.59; H, 5.35.
3.3.17 Potassium 4-vinylphenolate

Chemical Structure:

\[
\begin{array}{c}
\text{Synthesized} \\
\text{C}_8\text{H}_7\text{KO} \\
158.24 \\
\end{array}
\]

Source: Synthesized
Empirical Formula: \( \text{C}_8\text{H}_7\text{KO} \)
Molecular Weight, g/mol: 158.24

Synthesis Procedure:

a) 4-Acetoxystyrene (6.244g; 38.5 mmol) was added to a vial along with 70 ml of a 1.5 M KOH (0.105 mol KOH) solution and a magnetic stir bar. The mixture was purged with argon and heated to 35-40°C with vigorous stirring. Within 30 minutes, the interfacial mixture became homogeneous. Stirring continued at this temperature for a total of 1 hour.

b) Potassium 4-vinylphenolate could also be prepared from bis(4-vinylphenyl) carbonate (5.126g; 19.3 mmol) by cleavage in an interfacial mixture of 50 ml of methylene chloride and 80 ml of 1.5 M KOH. The interfacial mixture was refluxed for 5 hours under positive argon pressure to obtain 100% cleavage to the phenolate.

3.3.18 Phenylphosphonic dichloride

Chemical Structure:

\[
\begin{array}{c}
\text{Aldrich} \\
\text{C}_6\text{H}_5\text{Cl}_2\text{OP} \\
\end{array}
\]
Molecular Weight, g/mol: 194.99
Boiling Point, °C: 258/760
Density, g/ml 1.375

Purification Procedure:

Phenylphosphonic dichloride was used as received (97%).

3.3.19 Diphenylphosphinic chloride

Chemical Structure:

Source: Aldrich
Empirical Formula: C₁₂H₁₀ClO₃P
Molecular Weight, g/mol: 236.64
Boiling Point, °C/mm Hg: 222/16
Density, g/ml 1.240

Purification Procedure:

Diphenylphosphinic chloride was used as received (98%).

3.3.20 Bis(4-hydroxyphenyl)phenylphosphine oxide

Chemical Structure:

Source: Synthesized
Empirical Formula: \( \text{C}_{18}\text{H}_{15}\text{O}_3\text{P} \)

Molecular Weight, g/mol: 310.29

Melting Point, °C: 241-242

Synthesis Procedure:

The bis(4-hydroxyphenyl)phenylphosphine oxide used in this work was synthesized through the Grignard of 2-(4-bromophenoxy)tetrahydropyran. Mg turnings (8.99g; 0.37 mol) and a crystal of iodine were added to a dry, 3 neck, 2000 ml round bottom flask with condenser, mechanical stirrer, and addition funnel attached. The apparatus was flame dried under argon purge and a solution of 2-(4-bromophenoxy)tetrahydropyran (96.09g; 0.37 mol) in 400 ml THF was transferred to the addition funnel via cannula. The solution was added dropwise over 3 hours while cooling with a cold water bath. After 2 additional hours at room temperature, a solution of phenylphosphonic dichloride (26.50 ml; 0.187 mol) in 120 ml THF was added dropwise from the addition funnel while cooling with an ice bath. The reaction mixture warmed to room temperature and stirred for 8 hours at which time 50 ml methanol and 25 ml concentrated HCl were added. The solvent was then stripped by rotary evaporation to yield a brown viscous oil. The oil was dissolved in 600 ml 2.5M NaOH and washed with ether. The aqueous layer was precipitated into 1000 ml 2.5M HCl with vigorous stirring to yield a white precipitate. After filtering and drying under vacuum at 60°C overnight, the material was recrystallized from 80 ml methanol. The off-white crystals were filtered and recrystallized from 300 ml methanol to yield 45.04g (78% yield) of white crystals. Elemental analysis calculated for \( \text{C}_{18}\text{H}_{15}\text{O}_3\text{P} \): C, 69.68; H, 4.87. Found: C, 69.46; H, 4.82.
3.3.21 4-Bromoanisole

Chemical Structure:

Source: Aldrich

Empirical Formula: C7H7BrO

Molecular Weight, g/mol: 187.04

Boiling Point, °C/mm Hg: 223/760

Density, g/ml 1.494

Purification Procedure:

Anhydrous 4-bromoanisole was obtained and used as received.

3.3.22 4-Hydroxyphenyl diphenylphosphine oxide

Chemical Structure:

Source: Synthesized

Empirical Formula: C18H15O2P

Molecular Weight, g/mol: 294.29

Melting Point, °C: 248-249

Synthesis Procedure:

Mg turnings (1.97g; 81.0 mmol) and a crystal of I2 were added to a dry 3 neck, 500ml round bottom flask. A condenser, addition funnel, and overhead stirrer were attached and the flask was flame dried under argon flow. 4-Bromoanisole (10.14 ml; 81.0 mmol) was added to the addition funnel by
syringe followed by 50 ml THF which was also added by syringe. The 4-bromoanisole solution was added dropwise over 1 hour while cooling with a cold water bath. After 2 hours, diphenylphosphinic chloride (15.46 ml; 81.0 mmol) was added to the addition funnel and dissolved in 60 ml THF. This solution was added dropwise to the Grignard reagent while cooling with an ice bath. The reaction was warmed to room temperature and stirred for 12 hours. The reaction mixture was poured into 50 ml concentrated HCl and ice. The organic material was extracted with methylene chloride and the combined extracts were washed with water. The methylene chloride was removed by rotary evaporation to yield a slightly viscous, green oil. The oil was refluxed in 150 ml HBr (48% aqueous) and 150 ml acetic acid for 24 hours. The solution was poured over ice water and the resulting yellow solid was filtered and washed with water. The solid was recrystallized from 200 ml 95% methanol to yield 15.20 g (64% yield) of white crystals. Elemental analysis calculated for C_{18}H_{15}O_{3}P: C, 73.46; H, 5.14. Found: C, 73.23; H, 5.23.

3.3.23 Bis(triphenylphosphine oxide) carbonate

Chemical Structure:

![Chemical Structure](image)

Source: Synthesized

Empirical Formula: C_{37}H_{28}O_{5}P_{2}

Molecular Weight, g/mol: 614.57

Synthesis Procedure:
4-Hydroxyphenyl diphenylphosphine oxide (2.20 g; 7.50 mmol) was converted to the sodium phenolate in 22 ml 0.8 M NaOH. 20 ml methylene chloride was added along with triethylamine (0.17 ml; 1.20 mmol). Phosgene (2.2 g; 2.2 mmol) was introduced to the stirred mixture at a rate of 0.1 g/min. for 22 minutes. The methylene chloride layer was separated and washed twice with 0.5 M HCl followed by three times with water. The methylene chloride was evaporated to yield an oil which solidified to an amorphous solid. The solid was pulverized to yield 2.08 g (94% yield). Elemental analysis calculated for C₃₇H₂₈O₅P₂: C, 72.31; H, 4.59. Found: C, 72.16; H, 4.65.

3.3.24 Terephthaloyl chloride

Chemical Structure:

\[ \text{Cl} \quad \text{C} \quad \text{O} \quad \text{P} \quad \text{Cl} \]

Source: Aldrich
Empirical Formula: C₈H₄Cl₂O₂
Molecular Weight, g/mol: 203.02
Melting Point, °C: 79-81

Purification Procedure:

50 g of terephthaloyl chloride was dissolved into 130 ml of boiling hexanes. The solution was gravity filtered hot into a flask containing a small amount of boiling hexanes in order to remove acid impurities. The excess of hexanes was evaporated until terephthaloyl chloride started to crystallize from solution. 10 ml of hexanes was added and the solution was cooled slowly to room temperature followed by 1 hour in an ice bath. The crystals were filtered and dried at a reduced pressure of 1 mm Hg at room temperature to yield 42.11 g (84.2% yield).
3.3.25 Tetramethylammonium hydroxide pentahydrate

Chemical Structure:

\[
\text{CH}_3\text{OH}^-
\]

\[
\text{CH}_3\text{N}^+\text{CH}_3 \cdot 5\text{H}_2\text{O}
\]

Source: Aldrich
Empirical Formula: \( \text{C}_4\text{H}_{13}\text{NO} \cdot \text{H}_2\text{O} \)
Molecular Weight, g/mol: 181.23
Melting Point, °C: 65-68

Purification Procedure:

Tetramethylammonium hydroxide pentahydrate was protected from moisture and stored under argon.

3.3.26 Styrene

Chemical Structure:

Source: Aldrich
Empirical Formula: \( \text{C}_8\text{H}_8 \)
Molecular Weight, g/mol: 104.15
Melting Point, °C: 145-146
Density, g/ml 0.909

Purification Procedure:

Styrene was obtained as 99+% pure inhibited with 10-15 ppm \( t \)-butylcatechol. Purification was accomplished by distillation from calcium hydride in an ice cooled distillation flask with the application of a vacuum. The
receiver flask was cooled with dry ice, and the styrene was collected. The styrene was stored under argon in a septum sealed round bottom flask until use. The styrene was stored at -20°C and was kept for no longer than 1 week before requiring repurification.

3.3.27 α,ω-Dimethylamino-oligodimethylsiloxane

Chemical Structure:

\[
\begin{align*}
\text{N-Si-O(\text{Si-O})_{2-5}-\text{Si-N}}
\end{align*}
\]

Source: Petrarch:  
Molecular Weight, g/mol: 425-600 (DP = 2-5)  
Density, g/ml 1.02  
Purification Procedure:  
The silylamine endblocker was used as received from Petrarch.

3.3.28 4-(Tetrahydropyran-2-oxy-4-cumyl)sodium phenolate  
(Mono THP bisphenol A sodium salt)

Chemical Structure:

\[
\begin{align*}
\text{O-} - \text{O-} - \text{N}^+ \text{Na^+}
\end{align*}
\]

Source: Synthesized  
Empirical Formula: C20H23NaO3  
Molecular Weight, g/mol: 343.39  
Melting Point, °C: Decomposes at 203-205  
Synthesis Procedure:
Bisphenol A (10.00g; 43.8 mmol) and a catalytic amount of p-toluene sulfonyl acid monohydrate were dissolved in 100 ml THF. 3,4-2H-dihydropyran (4.42g; 52.5 mmol) was added to the solution over 45 minutes and stirred an additional 2 hours at 25°C. 80 ml of ethyl acetate was added to the mixture and the solution was washed with 100 ml of 2.5M NaOH and twice with water. The solvent was removed and the residue was redissolved in 100 ml of diethyl ether. The solution was cooled in an ice bath and a stoichiometric amount of 2.5M NaOH was added. White crystals of product immediately precipitated. The crystals were isolated by filtration and washed with ether to yield 5.84g (39%) of the expected monoprotected product.

3.4 Synthesis of Polymers and Oligomers

3.4.1 Synthesis of Polydimethylsiloxane Oligomers

3.4.1.1 THP and Phenol Terminated Oligomers

Tetrahydropyranyloxyaryl terminated polydimethylsiloxane oligomers were synthesized by a base catalyzed equilibration reaction between D4 and either of the synthesized silanol endblockers (THP-P-Silanol, THP-BP-Silanol). The average molecular weight of the oligomers was varied by changing the ratio of endblocker relative to the amount of D4. The tetrahydropyranyl protecting group could subsequently be removed to yield the corresponding phenol-terminated polydimethylsiloxane oligomers. The number average molecular weight of the polydimethylsiloxane oligomers was more conveniently represented by the degree of polymerization (DP) or the number of repeat units. As an example, the synthesis of a DP = 25 phenol terminated polydimethylsiloxane oligomer is described below:
Dimethyl-4-(tetrahydropyran-2-xyloxy)phenylsilanol (2.90g; 11.5 mmol) was combined with 9.0 mg (0.07 wt.%) tetramethylammonium hydroxide pentahydrate, and 5 ml of benzene in a 100 ml, 2 neck round bottom flask equipped with a Dean-Stark trap filled with benzene and a combination thermometer argon inlet adapter. A light argon flow was maintained throughout the reaction while stirring was effected with a magnetic stir bar. The flask was immersed in an oil bath at 85°C to remove the water by the distillation of the benzene/water azetrop. After 1 hour, D₄ (10.30 ml; 33.1 mmol) was added. After 10 hours, the benzene was completely distilled from the reaction mixture by removal of the benzene from the Dean-Stark trap. The reaction continued for 10 more hours at 80°C. The reaction product was dissolved in 100 ml of hexane, and the resulting solution was washed 3 times with 50 ml portions of water, dried over magnesium sulfate, filtered, and the hexane removed by rotary evaporation. The slightly viscous oil was placed on a high vacuum line at 0.3 mm Hg and heated to 80°C for 12 hours to remove residual solvent and cyclic siloxanes resulting in 10.23g (81%) yield of tetrahydropyranoxypheynyl terminated polydimethylsiloxane (THP-P-PSX).

The tetrahydropyranyl ether was cleaved under mild conditions. The oligomer was dissolved in 80 ml ether in a 2 neck 200 ml round bottom flask equipped with a condenser and thermometer. 80 ml of acetic acid and 40 ml of methanol were added and the reaction mixture was heated to reflux (35°C). Aliquots were periodically removed and analyzed by ¹H NMR to determine the extent of tetrahydropyranyl ether cleavage. Complete cleavage was attained after approximately 40 hrs. 100 ml of ether was added and the solution was washed twice with 50 ml portions of 1M NaHCO₃ and three times with water.
The ether solution was dried over MgSO₄, filtered and the ether removed by rotary evaporation. The product was placed on a high vacuum line at 0.3 mm Hg at 80°C for 12 hrs. to remove residual solvent and tetrahydropyranyl ether cleavage product. 8.49 g (92% yield) of phenol terminated polydimethylsiloxane oligomer (OH-P-PSX) was obtained.

A variety of molecular weights were synthesized by this method. Alternatively the biphenyl based silanol endblocker could be used under the same reaction conditions to synthesize the corresponding terminated oligomers (THP-BP-PSX and OH-BP-PSX).

3.4.1.2 Silylamine Terminated Oligomers

The silylamine endblocker was equilibrated with D₄ using tetramethyammonium hydroxide as catalyst. Different molecular weight oligomers were synthesized by altering the ratio of endblocker to D₄. An example redistribution reaction to form an oligomer with DP = 10 is demonstrated below:

A siloxanolate catalyst was prepared by reacting 30 mg (0.16 mmol) of tetramethylammonium hydroxide pentahydrate with 1.5 ml (4.8 mmol) of D₄ in a 100 ml, three neck round bottom flask equipped with a Dean-Stark trap, argon inlet, and mechanical stirrer. 10 ml of hexanes was added in order to azeotropically remove the water produced. The reaction mixture stirred at reflux for 12 hours after which time the hexanes was removed from the reaction mixture. The Dean-Stark trap was replaced with a condenser, and the silylamine endcapper (7.00g; 11.7 mmol) and D₄ (2.10 ml; 11.6 mmol) were added to the reaction flask. The reaction temperature was held at 80°C for 12
hours and then increased to 150°C to decompose the catalyst. The product was placed on a high vacuum line at 0.3 mm Hg and heated at 80°C for 12 hours to remove residual cyclic siloxanes, resulting in 8.35g (81%) yield of oligomer with DP = 9.9.

3.4.2 Molecular Weight Control in the Synthesis of Polycarbonates

The molecular weight of the homo- and copolycarbonates could be controlled through a simple offset of stoichiometry. Due to the interfacial nature of the reaction, and since the reaction involves the hydrolyzable chloroformate group, an excess of phosgene does not limit the molecular weight. The molecular weight can therefore be controlled by the addition of a monofunctional reagent such that the bisphenol is incorporated completely within the monofunctional endgroups. The desired molecular weight between end groups can be achieved by use of the following formulae:

\[ DP = \frac{<M_n>}{<M_0>} \]

\[ X = \frac{(2) \text{ (moles of monomer)}}{DP} \]

Where,

DP = number average degree of polymerization or number of repeating groups

\(<M_n> = \text{number average molecular weight desired} \)

\(<M_0> = \text{average molecular weight of repeat unit (254.29 g/mol for homopolycarbonate) } \)

X = the number of moles of monofunctional reagent

The value of \(<M_0>\) varies whether homo- or copolycarbonates are being synthesized. The value of \(X\) can be solved to determine the amount of monofunctional reagent required.
3.4.3 Synthesis of Phenol Terminated Polycarbonate Oligomers

Phenol terminated polycarbonate oligomers of controlled molecular weight were conveniently synthesized by the addition of a calculated amount of mono THP bisphenol A sodium salt to an interfacial polymerization followed by subsequent acid catalyzed cleavage of the protecting group. The projected molecular weights of the oligomers were calculated based on the above equations, while the actual molecular weight obtained was determined through UV-Vis spectroscopy by the method outlined in ref.\textsuperscript{183} An example polymerization for the synthesis of a 5.0 kg/mole oligomer is demonstrated below:

Bisphenol A (10.00g; 43.8 mmol) and mono THP bisphenol A sodium salt (1.703g; 4.96 mmol) were added to a 500 ml reaction flask depicted in Figure 3.4.3.1. 60 ml of water and 14 ml of 6.25M NaOH were added along with 100 ml of methylene chloride and 0.60 ml (4.4 mmol) of triethylamine. Phosgene (9.5g; 96 mmol) was added to the rapidly stirred interfacial mixture at a rate of 0.24 g/min for 40 minutes while maintaining the pH of the reaction mixture at 10-11 by the addition of 6.25M NaOH. At the end of this time, the layers were separated and the organic layer was washed twice with 0.3M HCl and twice with water. The solution was then refluxed with 0.1g of p-toluene sulfonic acid monohydrate for 2 hours. The solution was washed 4 times with water and the polymer isolated by flashing off the methylene chloride in rapidly stirred boiling water. The polymer was filtered and dried under vacuum to yield 11.16 g (90 %) of oligomer with $<M_n> = 4.7\text{ kg/mol}$ by UV-Vis. spectroscopic analysis.
Figure 3.4.3.1 Polycarbonate Polymerization Flask
3.4.4 Synthesis of Polycarbonate-Polydimethylsiloxane Copolymers

3.4.4.1 Perfectly Alternating Block Copolymers (Si—O—C Bonds)

Perfectly alternating block copolymers of polycarbonate and polydimethylsiloxane were prepared by the reaction between silylamine terminated polydimethylsiloxanes and phenol terminated polycarbonates in refluxing chlorobenzene. An example of the synthesis of a copolymer from a polycarbonate oligomer with a $<M_n>$ value of 4.7 kg/mole and a polydimethylsiloxane oligomer with a $<M_n>$ value of 0.88 kg/mol (DP = 9.9) is demonstrated below:

1.342g (0.285 mmol) of phenol terminated polycarbonate and 6.80 mg (4.52 x $10^{-2}$ mmol) of 4-t-butylphenol were added to a 100 ml, 2 neck round bottom flask equipped with a Dean-Stark trap and argon inlet. 30 ml of chlorobenzene was added and 10 ml were subsequently removed by distillation. The silylamine terminated oligomer (0.288g; 0.328 mmol) was dissolved in 5 ml of chlorobenzene and added to the refluxing reaction mixture. Dimethylamine was immediately observed as a reaction byproduct. The reaction continued at reflux for 3 hours after which time the copolymer was isolated by precipitation in methanol. The product was filtered and dried under vacuum to yield 1.45g (90%).

3.4.4.2 In Situ Random Block Copolymers (Si—Aryl Bonds)

Copolymers of various compositions were synthesized. The weight percent and number average block length of polydimethylsiloxane, as well as the type of functionalization (phenyl or biphenyl) were varied. The molecular weight ($<M_n>$) of the copolymers was controlled to approximately 30.0 kg/mole through
the addition of 4-t-butylphenol in the reaction mixture. A representative synthetic procedure is described below for a copolymer containing 30 weight percent (DP = 21) polydimethylsiloxane:

A 5 neck 500 ml reaction flask such as that shown in Figure 3.4.3.1 was utilized. Bisphenol A (4.20g; 18.4 mmol), the polydimethylsiloxane oligomer (1.80g; 1.02 mmol), and 4-t-butylphenol (63.7 mg; 0.424 mmol) were added to the flask along with 38 ml of water and 50 ml of methylene chloride. Triethylamine (1.0 ml; 7.2 mmol) was added at 38 mole percent relative to bisphenol. The pH was adjusted to 10.5 by the addition of 6.25M NaOH. Phosgene (5.8g; 58 mmol) was introduced to the rapidly stirred mixture at a rate of 0.2 g/min. for 28 minutes while maintaining the pH between 9.5 and 10.5 through the metered addition of 6.25M NaOH. At the end of this time, the flask was purged with argon for 10 minutes to remove excess phosgene. The layers were separated, and the organic layer was washed twice with 0.3M HCl and 5 times with water. The copolymer was isolated by the addition of the solution to 500 ml of rapidly stirred hexanes. The precipitated polymer was filtered and dried at 60°C and a reduced pressure of 1mm Hg for 12 hours.

3.4.4 Synthesis of Vinylphenyl Terminated Polycarbonate Oligomers

Vinylphenylcarbonate terminated polycarbonate oligomers of different molecular weights were synthesized by two different procedures. Each procedure is described below for a \(<M_n> \approx 5.0 \text{ kg/mol}\) sample. Adjustment of the stoichiometry as demonstrated in section 3.4.2 was done in order to synthesize other molecular weight samples.
3.4.4.1 Conventional Route to Polycarbonate Oligomers (Method A)

Bisphenol A (90.00g; 0.394 mol) was added to the 5 neck, 2000 ml reaction flask depicted in Figure 3.4.3.1, along with 500 ml of water, 79 ml of 10M NaOH, and 600 ml of methylene chloride. The potassium 4-vinylphenolate solution prepared in section 3.3.17 was then added to the interfacial mixture followed by triethylamine (8.8 ml; 63 mmol). Phosgene (78g; 0.78 mol) was introduced to the rapidly stirred mixture through a teflon tube below the liquid surface at the rate of 0.65 g/min for 120 minutes while maintaining the pH at 10.5 -11.0 by the metered addition of 10M NaOH. The mixture was then purged with argon and the polymer solution was separated from the aqueous layer. The methylene chloride layer was washed twice with 0.5M HCl and 5 times with water. The methylene chloride was then flashed off by slowly adding the solution to rapidly stirred boiling water in a Waring commercial blender. The polymer powder was filtered and dried at 60°C under vacuum to yield 97.11g (96%).

3.4.4.2 Chloroformate Route to Polycarbonate Oligomers

Bisphenol A (90.00g; 0.394 mol) was added to the 5 neck, 2000 ml reaction flask depicted in figure 3.4.3.1. 600 ml water and 79 ml of 10M NaOH were added, and the mixture was stirred while purging with argon until the bisphenolate was formed and the resulting pH was approximately 11.6. 360 ml of methylene chloride was then added. Phosgene (78g; 0.79 mol) was introduced into the flask at the rate of 1.0 g/min. for 78 minutes while stirring vigorously. As phosgene was added the pH slowly decreased, but was
maintained at 9.5 by the dropwise addition of 10M NaOH. The reaction mixture was purged with argon for 10 minutes to displace unreacted phosgene. At this time an aliquot was removed for analysis. The potassium 4-vinylphenolate solution prepared in section 3.3.17 was added to the mixture and washed in with 100 ml of water and 240 ml of methylene chloride. The pH was adjusted to 11.0 and triethylamine (8.8 ml; 63 mmol) was added to the rapidly stirred mixture. The pH immediately began to drop and was adjusted to 11.0 by the addition of 10 M NaOH. The mixture was stirred for 1 hour, after which phosgene was reintroduced at the rate of 0.55 g/min for 30 minutes while maintaining the pH at 11.0 to complete the reaction. The reaction mixture was then purged with argon for 15 minutes, and the layers were then separated. The polymer solution was worked up and isolated as in section 3.4.4.1. The isolated white polymer powder was dried for 12 hours at 60°C and a reduced pressure of 1mm Hg to yield 96.32g (95% yield).

3.4.5 Preparation of Polycarbonate Networks

Polycarbonate networks were prepared by the thermal cure of the vinylphenyl terminated oligomers to obtain samples with different dimensions. Films were prepared either by compression molding followed by curing at elevated temperatures or by the subsequent oven curing of solution cast oligomeric films. Plaques 75mm x 40mm x 3.2 mm were molded from the vinylphenyl terminated polycarbonate oligomers by the repeated filling of a stainless steel mold of these dimensions. The different oligomers were compression molded on a PHI Melt Press at different temperatures ranging from 120°C - 180°C, depending on the molecular weight of the oligomer. The
oligomers were then thermally cured without added initiator at temperatures from 180°C - 300°C for different lengths of time at 10000 - 20000 pounds of pressure.

The polycarbonate oligomers were also used to synthesize networks with other vinyl monomers. Polycarbonate oligomers were dissolved in styrene at levels of up to 25 weight percent. The mixtures were sealed in vials and purged with argon. The samples were cured at 120°C for 1 hour, followed by 1 hour at 150°C, and 6 hours at 200°C.

3.4.6 Synthesis of Phosphorus Containing Polyarylate

The polyarylate from bis(4-hydroxyphenyl)phenylphosphine oxide and terephthaloyl chloride was synthesized by interfacial techniques. The polymer was synthesized to a controlled molecular weight (<M_n>) of 40.0 kg/mol by the addition of t-butylphenol, and was also synthesized without added monofunctional reagent. An example of this polymerization is described below: Bis(4-hydroxyphenyl)phenylphosphine oxide (4.00g; 12.9 mmol) and t-butylphenol (42.7 mg; 0.280 mmol) were placed in a 500ml, 3 neck round bottom flask equipped with an overhead mechanical stirrer, addition funnel, and condenser. The bisphenolate was formed and dissolved in 40 ml of 0.7M NaOH. 10 ml of methylene chloride and tetraethylammonium bromide (1.00g; 4.76 mmol) were added to the flask, and the mixture was rapidly stirred. Freshly recrystallized terephthaloyl chloride (26.46 mg; 13.0 mmol) was added to the addition funnel and dissolved in 30 ml of methylene chloride. The terephthaloyl chloride solution was added all at once from the addition funnel and washed into the reaction mixture with two 10 ml portions of methylene chloride. The
mixture stirred for 1 hour, after which the layers were separated. The polymer solution was worked up and the polymer isolated as in section 3.4.4.1 to yield 4.86g (85% yield).

3.4.7 Synthesis of Phosphorus Containing Polycarbonate Copolymers

Copolymers containing different amounts of bis(4-hydroxyphenyl)phenylphosphine oxide were synthesized. The amount of phosphorus monomer added was calculated based on the weight percent of the repeat unit. The amount was varied from 0 to 100 weight percent of the repeat unit. A procedure for the synthesis of a copolymer containing 10 weight percent of the triphenylphosphine oxide carbonate repeat unit is represented below:

Bisphenol A (42.050g; 0.184 mol), bis(4-hydroxyphenyl)phenylphosphine oxide (4.614g; 0.015 mol), and t-butylphenol (0.7574g; 5.00 mmol) were added to a 5 neck, 2000 ml reaction flask depicted in Figure 3.4.3.1. 400 ml of water and 40 ml of 1.5 M NaOH were added. Once dissolution had occurred, triethylamine (4.4 ml; 32 mmol) and 400 ml of methylene chloride were added. Phosgene (30g; 0.30 mol) was introduced to the rapidly stirred interfacial mixture at the rate of 0.33 g/min. for 90 minutes while maintaining the pH at 11.0 by the metered addition of 1.5M NaOH. After this time, the reaction vessel was purged with argon for 15 minutes, and the layers were separated. The polymer solution was worked up and isolated as in 3.4.4.1. After drying at 85°C under vacuum for 12 hours, 48.40 g (95% yield) of copolymer was obtained.
3.4.8 Synthesis of Triphenylphosphine Oxide Terminated Polycarbonates

Bisphenol A polycarbonate was synthesized with 4-hydroxyphenylidiphenylphosphine oxide added as the monofunctional reagent. The substitution of this compound for the t-butylphenol normally used resulted in the formation of triphenylphosphine oxide terminal groups. Polycarbonates with targeted \( <M_n> \) of 15.0 kg/mole and 20.0 kg/mole were synthesized. The procedure used for the synthesis of a 20.0 kg/mol polymer was the same as that described in section 3.4.7 except for a few modifications. The amount of bisphenol A added was 50.00g (0.219 mol), and no bis(4-hydroxyphenyl)phenylphosphine oxide or t-butylphenol were used; 4-hydroxyphenylidiphenylphosphine oxide (1.5774g; 5.35 mmol) instead was added as an endcapper. 50.96g (92% yield) of polymer was isolated from the reaction.

3.5 Characterization

3.5.1 Intrinsic Viscosity \([\eta]\)

Intrinsic viscosities \([\eta]\) were measured in chloroform at 25°C with a Cannon-Ubbelohde viscometer having a bore size of 50 mm. After obtaining the flow time for pure solvent \((t_0)\), the flow times were measured for solutions of different concentration \((t)\). Initial polymer solutions were prepared by dissolving 0.200g of polymer in 20.0 ml of chloroform. 8.0 ml of the filtered solution was added to the viscometer and the flow time recorded. The solution was then diluted and the procedure repeated. At least three different concentrations were measured. The following relationships were used to calculate the intrinsic viscosity:
\[ \eta_{\text{rel}} = \eta_0 \]
\[ \eta_{\text{sp}} = (t-t_0)/\eta_0 \]
\[ \eta_{\text{inh}} = (\ln \eta_{\text{rel}})/c \]
\[ \eta_{\text{red}} = \eta_{\text{sp}}/c \]

Both the \( \eta_{\text{red}} \) and the \( \eta_{\text{inh}} \) were plotted versus concentration. The intrinsic viscosity \( [\eta] \) was determined as the average of the intercepts from the extrapolation of both lines to zero concentration.

3.5.2 Gel Permeation Chromatography (GPC)

Samples of oligomers, polymers, and copolymers were analyzed on a Waters GPC instrument equipped with a differential refractive index detector using chloroform as the solvent. Molecular weights were determined relative to polystyrene or polydimethylsiloxane standards. Samples were measured at a flow rate of 1.0 ml/min. and a temperature of 30°C.

3.5.3 Nuclear Magnetic Resonance (NMR)

3.5.3.1 Proton (\( ^{1}H \)) NMR

Solution \( ^{1}H \) NMR spectra were measured on a Varian 400 MHz instrument in CDCl\(_3\), deuterated acetone, D\(_2\)O, or deuterated DMSO depending on the solubility of the material. Structure of both low molecular weight, and oligomeric and polymeric compounds could be determined from the obtained spectra. \( ^{1}H \) NMR was also used to determine the number average molecular weights (\( <M_n> \)) of end-functionalized oligomers and polymers. The degree of
polymerization (DP) of oligomers and polymers were determined by finding the ratio of the integrated end group resonances relative to those of the backbone. The \(<M_n>\) (not including the end groups) could then be found by multiplying the DP by the molecular weight of the repeat unit. Addition of the molecular weight of the endgroups would give the total number average molecular weight. This is represented by the following formulae:

\[
\begin{align*}
DP &= \frac{\text{integrated backbone resonance}}{\# \text{ of protons in one repeat unit}} \\
&\quad \times \frac{\text{integrated end group resonance}}{\# \text{ of protons for both chain ends}} \\
<M_n> &= \text{(DP)} \times \text{(molecular weight of repeat unit)} \\
<M_n> \text{ total} &= <M_n> + \text{molecular weight of endgroups}
\end{align*}
\]

In this work, the total molecular weight including endgroups is the value usually reported and is represented simply by \(<M_n>\).

3.5.3.2 Phosphorus \((^{31}\text{P})\) NMR

Solution phosphorus \((^{31}\text{P})\) NMR spectra were obtained on a Varian 400 MHz instrument relative to 85% phosphoric acid. The same deuterated solvents used for \(^1\text{H}\) NMR samples were implemented. \(^{31}\text{P}\) NMR was used to determine purity, incorporation, and sequence distribution.
3.5.4 Differential Scanning Calorimetry (DSC)

Glass transition temperatures (Tg) and cure temperatures were determined with a Perkin Elmer Series 7 DSC. Samples were either powder or films contained in sealed aluminum pans. Measurements were made from 30°C to 250-400°C at a scanning rate of 10°C/min. under nitrogen. Second and third scans were performed on some samples by heating to the desired temperature in the previous scan and quench cooling to room temperature before reanalysis.

3.5.5 Dynamic Thermogravimetric Analysis (TGA)

Thermal stabilities and char yields were determined by thermogravimetric analysis (TGA) on a Perkin Elmer Series 7 instrument. A heating rate of 10°C/min. in an air atmosphere was used to analyze samples. Samples were measured to a temperature greater than 750°C to determine the residual char at elevated temperatures. The temperature at which 5% of the initial weight had been lost was compared for different samples to determine relative thermal stabilities.

3.5.6 Tensile Stress-Strain Measurements

The tensile tests were performed on an Instron 1123 equipped with a strain gauge extensometer (Instron 2630-013). 5-10 dog-bone shaped samples (ASTM D-638 #5) were cut from compression molded films with thicknesses from 3-10 mils. The samples were tested at room temperature using a crosshead speed of 0.5 in./min. consistent with ASTM D-638. The results of statistically consistent samples were averaged to determine the values.
3.5.7 Fracture Toughness ($K_{1C}$) Sample Preparation and Measurement

Fracture toughness measurements were conducted in accordance with ASTM D-5045-91 (E-399-90). 10 - 12 $K_{1C}$ test samples with dimensions 6mm x 40mm x 3 mm were cut from the plaques prepared in section 3.4.5 on a Craftsman Scroll Saw. The individual samples were notched at the center to a depth of approximately 0.5mm with the reciprocating saw. Sharp cracks were then initiated by gently tapping a liquid nitrogen cooled razor blade within the notch, taking care to insure that the crack had evenly propagated into the sample. The pre-cracked samples were then loaded on a three-point-bend fixture attached to an instron and tested at a rate of 0.05 in/min.

3.5.8 Dynamic Mechanical Analysis (DMA)

DMA analyses were performed on a Perkin Elmer DMA-7 analyzer in the three-point-bending mode. Tests were conducted on the fracture toughness samples at a frequency of 1Hz under a dynamic temperature scan rate of 5°C/min.

3.5.9 Fourier Transform Infrared (FTIR) Spectroscopy

FTIR was performed on samples using a Nicolet Impact 400 spectrometer. Samples were either cast from solution onto sodium chloride salt plates or silicon wafers. The spectra were observed and recorded in absorbance mode.
3.5.10 Solvent Resistance Properties

3.5.10.1 Scanning Electron Microscopy (SEM)

The fracture surface of the broken fracture toughness samples were exposed to solvent for different amounts of time. The morphology of the fracture surface was determined with an International Scientific Instruments Model SX-40 SEM. Samples were mounted on aluminum substrates with silver paint and the fracture surface was sputtered with approximately 100Å gold film from a Bio Rad Polaron Model E 4500 sputter coater. Samples were observed at 2000, 5000, and 10000 X magnification.

3.5.10.2 Solvent Extraction Studies

Cured samples with dimensions of 6mm x 20mm x 3.2 mm were extracted with chloroform for 4 days using a soxhlet extraction apparatus. The amount of extracted material was measured by evaporating the chloroform from the tared flask, and re-weighing the flask containing the extracted material to determine the percent of soluble products.

3.5.10.3 Swelling Experiments

Swelling experiments were performed on samples with the dimensions of approximately 6mm x 20mm x 3.2mm and cured under similar conditions. The cured samples were weighed and placed in 1,1,2,2-tetrachloroethane at 25°C for 24 hours. After this time the swollen samples were weighed to determine the solvent uptake. The samples were then dried under vacuum for 24 hours at 50°C, reweighed and the process repeated.
3.5.11 Cone Calorimetry

Phosphorus containing copolymer samples with dimensions of 10 cm x 10 cm x 3 mm were compression molded and sent to the Fire Research Laboratory of the National Institute of Standards and Technology (NIST) where they were evaluated by cone calorimetry under a constant heat of 40 kW/m². The heat release rate over time was compared and evaluated.

3.5.12 Single Lap Shear Determination of Adhesive Bond Strengths

The adhesive bond strengths of crosslinked polycarbonates to aluminum was examined by performing single lap shear tests at 25°C according to ASTM D-1002. Aluminum coupons with dimensions 1in. x 5in. x 1.5mm were prepared according to ASTM D-2651-79 with a sulfuric acid/dichromate etch. A primer coating of 5 weight percent polymer in chloroform was applied to the surface of the coupons. Melt pressed films of reactively terminated oligomers were formed by compression molding at 160 - 190°C for 5 minutes. The "pre-cured" films were placed between aluminum coupons in a single lap shear orientation and cured at 500 pounds of pressure and at 180 - 220°C for 30 or 60 minutes. The samples were tested on an Instron Model 1123 at a crosshead speed of 0.05in./min. Single lap shear samples were similarly prepared of non-reactively terminated polycarbonates for comparison.
4.0 RESULTS AND DISCUSSION

4.1 Polycarbonate-Polydimethylsiloxane Copolymers

The useful properties of polydimethylsiloxane homopolymers are listed in Table 4.1.1. Copolymers of polydimethylsiloxane have been widely studied for a number of years because of the idea that these useful properties of polydimethylsiloxane can be imparted to the copolymer.

- Low surface energy
- High compressibility
- Biological inertness
- Atomic oxygen resistance
- Low temperature flexibility
- Low polarity (hydrophobicity)
- Thermal and oxidative stability
- Ultraviolet radiation resistance
- High permeability to small molecules
- Low viscosity for a given molecular weight
- Minimum change in viscosity with temperature
- Broad service temperature range due to low Tg

Table 4.1.1 Physical Properties of Polydimethylsiloxanes

Copolymers of polycarbonate and polydimethylsiloxane are commercial materials which have been synthesized predominately for their improved low temperature impact properties over bisphenol A polycarbonate. A number of
applications have been found for these materials including their use in the manufacture of bulletproof materials.\textsuperscript{184} The polydimethylsiloxane has also been found to increase the fire resistance properties,\textsuperscript{102} and the selective gas permeability of the copolymers.\textsuperscript{185} Although many such useful properties can be realized for these materials, improvements in the basic structure have been sought. The commercial materials contain hydrolytically unstable Si—O—C bonds between blocks which is a potential drawback of these useful materials.

The objective of the work presented here was to synthesize functionalized polydimethylsiloxane oligomers which could be incorporated into polycarbonates yielding Si—C bonds rather than Si—O—C bonds. This is not a new concept, since others have attempted to synthesize functionalized polydimethylsiloxane oligomers with the more hydrolytically stable Si—C bonds, and these approaches have been reviewed in section 2.2.4. The present work concentrated on the synthesis of phenol functional polydimethylsiloxane oligomers with Si—aryl linkages so that thermally and hydrolytically stable copolymers could be produced. A series of copolymers with different compositions were synthesized and examined, and the improvement in the properties was observed.

4.1.1 Synthesis of Phenol Terminated Polydimethylsiloxane Oligomers

The approach taken in this research allows for the synthesis of a wide range of oligomer molecular weights through well established base catalyzed redistribution reactions. This was accomplished by the synthesis of properly functionalized dimethylsilanols containing Si—aryl bonds, which could be used
as endcappers in the synthesis of functionally terminated oligomers. Two such functionalized dimethylsilanols were synthesized starting with 4-bromophenol and 4-(4-bromophenyl)phenol by the sequence of reactions shown in Scheme 4.1.1.1. The aromatic hydroxyl group of the hydroxyaryl bromides was protected through the formation of the tetrahydropyranyl (THP) ether.\textsuperscript{182} The silanols were then synthesized through the formation of Grignard reagents of the THP protected hydroxyaryl bromides which could be reacted with a stoichiometric amount of dichlorodimethylsilane and subsequently hydrolyzed.

\[
\begin{align*}
\text{oxygen} + \text{HO-Ar-Br} & \rightarrow \text{oxygen-O-Ar-Br} \\
\text{oxygen-O-Ar-Br} + \text{Mg} & \rightarrow \text{oxygen-O-Ar-MgBr} \\
\text{oxygen-O-Ar-MgBr} + \text{Cl-Si-Cl} & \rightarrow \text{oxygen-O-Ar-Si-Cl} & \text{(THF; 0°C)} \\
\text{oxygen-O-Ar-Si-Cl} & \rightarrow \text{oxygen-O-Ar-Si-OH} & \text{(1M NaHCO}_3/\text{ether)} \\
\end{align*}
\]

\(\text{Ar} = \begin{array}{c}
\text{phenyl} \\
\text{biaryl}
\end{array}\)

\textbf{Scheme 4.1.1.1} Synthesis of Tetrahydropyranoyloxyaryl dimethylsilanols
The synthesis of the functionalized dimethylsilanols was a modification of the method of Matsukawa, et al.\textsuperscript{177} They found it necessary to have triethylamine present during the hydrolysis of the silylchloride to the silanol so that premature coupling to the disiloxane could be avoided. In their work, the THP protecting group was cleaved during subsequent acid catalyzed coupling to the disiloxane and removal of the triethylamine hydrochloride. Cleavage of the protecting group at this step to regenerate the phenol did not allow for the subsequent base catalyzed redistribution to higher molecular weight oligomers. By retaining the protecting group, the functionalized silanols could be used to form oligomers of various molecular weights.

An attempt was made in this work to retain the protecting group and equilibrate to higher molecular weights. It was found that the titration of the HCl formed during hydrolysis of the silylchloride could be accomplished very efficiently by performing the hydrolysis in the presence of an aqueous NaHCO\textsubscript{3} solution, eliminating the need for triethylamine. This method of hydrolysis is known in the literature for the formation of silanols from silylchlorides.\textsuperscript{9,186} The silanols could thus be obtained in approximately 70 percent yield with the THP group intact. The $^1$H NMR spectra of each of the silanols (THP-P-Silanol, THP-BP-Silanol) are represented in Figures 4.1.1.1 and 4.1.1.2, respectively.
Figure 4.1.1.1 $^1$H NMR Spectrum of THP-P-Silanol (400 MHz, CDCl$_3$)
Figure 4.1.1.2 $^1$H NMR Spectrum of THP-BP-Silanol (400 MHz, CDCl$_3$)
The presence of the THP protecting group allowed for the use of the silanols in the base catalyzed equilibration with octamethylcyclotetrasiloxane (D₄) to form oligomers of various block lengths. The stability of this protecting group to basic conditions is well known. The equilibration reaction was conveniently carried out using tetramethylammonium hydroxide pentahydrate as catalyst. The reaction is demonstrated in Scheme 4.1.1.2. Either silanol could be used and coupled to form the respective disiloxane *in situ* under the base catalyzed reaction conditions. A solvent such as benzene was used to remove the water formed during the coupling, as well as that present in the hydrate of the catalyst, by the formation of the benzene/water azeotrope (bp = 69.25°C \(^{187}\)). The benzene was removed from the reaction in order to decrease the amount of cyclics formed at equilibrium, since it is well known that the presence of solvent increases the equilibrium yield of cyclics.\(^8,^{123}\) The 10-20% cyclics which were formed could be easily removed by vacuum distillation after removal or deactivation of the catalyst. Catalyst removal or deactivation was required since otherwise redistribution reactions could continue to form the equilibrium mixture of cyclics and linear oligomers.
Alternatively, either disiloxane could be prepared and isolated from the same base catalyzed conditions in the absence of D$_4$. The disiloxanes were crystalline mixtures of the isomers and could be used in the equilibration reactions after isolation. The formation of the disiloxanes in situ eliminated the need for their isolation.

The tetrahydropyranyl protecting group was very useful since it is well known that the cleavage of this acetal to regenerate the phenol can be accomplished under relatively mild acidic conditions.$^{133}$ Mild acidic cleavage conditions are required since the siloxane chain is not stable to strong acids.
Furthermore, the Si—aryl bond is not very stable under strong acid conditions. Protodesilation, demonstrated in Scheme 4.1.1.3, is known to occur for Si—aryl compounds, resulting in substitution of the SiR3 group by a proton. Although this reaction is more difficult when the SiR3 group is a siloxane, the presence of an electron donating para OH group can cause this reaction to occur quite readily. The biphenyl based systems were used in an attempt to possibly circumvent this instability, since it is known that in linear free energy terms, the effect of substituents on the protodesilation of biphenyle is four times smaller than for benzene.

![Scheme 4.1.1.3 Protodesilation of Si—Aryl Compounds](image)

Either phenyl or biphenyl linked oligomers could be used if mild enough THP cleavage conditions could be found. The cleavage of the protecting group by acetic acid at low temperatures was found to be effective in regenerating the phenol while leaving the Si—aryl bond intact. The cleavage is demonstrated in Scheme 4.1.1.4. The methyl-2-tetrahydropyranyl ether byproduct was easily removed from the hydroxyaryl terminated oligomers by vacuum distillation.
Dilute HCl was also used to cleave the protecting group, but was found to cause protodesilation when acid concentration or temperature was too high. Forcing conditions with acetic acid at higher temperature also caused protodesilation to occur. Other cleavage conditions and other acid catalysts were examined, but all resulted in small amounts of Si—aryl bond cleavage byproducts.

Oligomers of different block lengths were synthesized by offsetting the stoichiometry of Di relative to the silanol endcapper. The redistribution causes ring opening of the Di such that the average number of repeat units in the oligomer is dictated by the amount of endcapper present. The relative amounts of Di to endcapper required can be calculated in order to synthesize the desired DP. This can be done simply by using the following relationships and equations:
\[ \text{DP} = \text{desired block length} \]

\[ <M_n>_{dsx} = \text{molecular weight of THP protected disiloxane} \]

\[ <M_n>_{dsx} = 486.82 \text{ g/mol for THP-P-DSX} \]

\[ <M_n>_{dsx} = 639.01 \text{ g/mol for THP-BP-DSX} \]

\[ \text{grams of oligomer desired} = \text{moles of repeat unit} \]

\[ = \frac{\text{moles of repeat unit}}{[(75.14) + (M_{\text{dsx}}/ \text{DP})]} \]

\[ \text{moles of repeat unit} \]

\[ \text{moles of D}_4 = \frac{\text{4}}{\text{moles of repeat unit}} \]

\[ \text{moles of disiloxane} = \frac{\text{moles of repeat unit}}{\text{DP}} \]

\[ \text{moles of silanol} = \frac{\text{moles of disiloxane}}{2} \]

Knowing the moles of repeat unit, the moles of D4 required can be calculated since there are 4 moles of repeat unit produced from every mole of D4 ring-opened. The moles of disiloxane required is equivalent to the average number of oligomers produced (given that every oligomer is endcapped), and is obtained by dividing the number of moles of repeat unit by the number of repeat units (DP). Since two moles of silanol are utilized to produce one mole of disiloxane (or larger oligomer), the required amount of silanol can be easily calculated.

Since the reaction is a redistribution, no volatiles are given off (once the disiloxane is formed); therefore, the weight of the oligomer obtained is equal to

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that of the disiloxane plus D₄. The formation of an equilibrium amount of cyclics affects the DP and the weight of functionalized oligomer actually achieved. The DP will be decreased from that calculated since some of the siloxane is not incorporated into the linear oligomer. Corrections can be made in the relative amounts of D₄ to endcapper if an equilibrium amount of cyclics produced (=15%) is assumed. Adding a 15% excess of D₄ would therefore yield an oligomer with a DP closer to the theoretical.

4.1.2 Characterization of Polydimethylsiloxane Oligomers

¹H NMR spectra of typical THP-P-PSX and THP-BP-PSX oligomers are shown in Figures 4.1.2.1 and 4.1.2.2. The number average molecular weight (<Mₙ>) of the oligomers could be determined by ¹H NMR. For the polydimethylsiloxane oligomers, the resonance at 0.33 ppm (or 0.37 ppm) is due to the 12 methyl protons attached to the Si bonded to the phenyl (or biphenyl) group, while the resonance at 0.08 ppm is due to the methyl protons attached to the Si of the dimethylsiloxane backbone. The number of repeat units (DP) can be found by the following formula:

\[
DP = \frac{\text{integrated resonance at 0.08}}{6} \div \frac{\text{integrated resonance at 0.33 (or 0.37) ppm}}{12}
\]

Multiplying by the molecular weight of the repeat unit (74.15 g/mole) yields the <Mₙ> of the oligomer between the endgroups. The total number average molecular weight can be obtained by adding the molecular weight of the respective disiloxane to account for the functionalized end groups.
Figure 4.1.2.1 $^1$H NMR Spectrum of THP-P-PSX (400 MHz, CDCl$_3$)
Figure 4.1.2.2 $^1$H NMR Spectrum of THP-BP-PSX (400 MHz, CDCl$_3$)
Figure 4.1.2.3 $^1$H NMR Spectrum of OH-P-PSX (400 MHz, CDCl₃)
Figure 4.1.2.4 $^1$H NMR Spectrum of OH-BP-PSX (400 MHz, CDCl$_3$)
Cleavage of the THP protecting group and removal of the methyltetrahydropranyl ether byproduct was monitored by \(^1\)H NMR. The \(^1\)H NMR spectra of OH-P-PSX and OH-BP-PSX are shown in Figures 4.1.2.3 and 4.1.2.4, where the protecting group resonances present in Figures 4.1.2.1 and 4.1.2.2 are observed to disappear. The DP of the oligomers before and after cleavage was found to be identical while no cleavage of the Si—aryl bond could be detected under the acetic acid cleavage conditions. Under some of the more vigorous cleavage conditions examined, cleavage of the Si—aryl bond could be detected.

Although the biphenyl group was chosen to separate the electron donating properties of the O from the Si—aryl bond in order to achieve a more acid stable linkage, no exceptional increase in stability over the phenyl group was found. Synthesis of a functionalized endcapper from 3-bromophenol was attempted in order to separate the resonance electron donating effect of the -O- on the Si—aryl bond. Unfortunately, this route was not examined completely since the functionalized dimethylsilanol product obtained was an oil, making purification difficult.

Gel permeation chromatography (GPC) was used to further characterize the molecular weight and polydispersity of the oligomers, as well as the change in apparent molecular weight after cleavage. The molecular weights were determined relative to monodisperse polydimethylsiloxane standards, and the results are listed in Tables 4.1.2.1 (OH-P-PSX oligomers) and 4.1.2.2 (OH-BP-PSX oligomers) for comparison with those obtained by \(^1\)H NMR. The molecular weight by GPC before and after cleavage of the THP protecting group for two oligomers is represented in Table 4.1.2.3.
### Table 4.1.2.1 Molecular Weight Characterization of OH-P-PSX Oligomers

<table>
<thead>
<tr>
<th>DP</th>
<th>$&lt;M_n&gt;$ (kg/mol)</th>
<th>$&lt;M_n&gt;$ (kg/mol)</th>
<th>$&lt;M_w&gt;$ (kg/mol)</th>
<th>$&lt;M_w&gt;/&lt;M_n&gt;$</th>
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<td>13</td>
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### Table 4.1.2.2 Molecular Weight Characterization of OH-BP-PSX Oligomers

<table>
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<th>DP</th>
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<th>$&lt;M_n&gt;$ (kg/mol)</th>
<th>$&lt;M_w&gt;$ (kg/mol)</th>
<th>$&lt;M_w&gt;/&lt;M_n&gt;$</th>
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### Table 4.1.2.3 GPC Data Before and After THP Cleavage

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<th>THP-P-PSX</th>
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114
<table>
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<th>GPC (relative to polydimethylsiloxane stds.)</th>
<th>GPC (relative to polydimethylsiloxane stds.)</th>
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<tr>
<td>(&lt;M_n&gt;)</td>
<td>(&lt;M_w&gt;)</td>
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<td>1.4</td>
</tr>
<tr>
<td>4.0</td>
<td>5.1</td>
</tr>
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</table>

The polydispersities were found to be fairly narrow for the synthesized oligomers with values of 1.2 - 1.5. The \(<M_n>\) values of the phenol functional oligomers obtained by GPC generally agreed with those determined by \(^1\text{H}\) NMR. The values obtained for the OH-P-PSX oligomers by GPC also agreed fairly well with the THP-P-PSX oligomers before cleavage of the THP protecting group, reinforcing the \(^1\text{H}\) NMR data. The \(<M_n>\) values obtained by \(^1\text{H}\) NMR were considered to be more reliable numbers and were used in all subsequent calculations.

### 4.1.3 Synthesis of Polycarbonate-Polydimethylsiloxane Copolymers

The incorporation of the phenol-terminated polydimethylsiloxane oligomers into bisphenol A polycarbonates was accomplished under triethylamine catalyzed interfacial polymerization conditions. The polycarbonate blocks within the copolymer were produced \textit{in situ}. This type of a reaction is known to produce a distribution of block lengths of each component.\(^{136}\) Given equal reactivities of the two bisphenol components, random reactions should result in some coupling of the polydimethylsiloxane oligomers. If the reactivities of the two components are very different, a large amount of blockiness different from
that expected from random reactions can occur. This can result in undesirable macrophase separated materials if the block sizes become very large. For the compositions synthesized here, no macrophase separation could be detected even when starting with large polydimethylsiloxane blocks, as evidenced by the fact that all solution cast films resulted in transparent materials. From this result, it can be concluded that the reactivities of the phenol-functional polydimethylsiloxanes are similar to that of the bisphenol A under the conditions used.

Copolymers were synthesized from both OH-P-PSX and OH-BP-PSX. Series of copolymers with varying weight percent polydimethylsiloxane and varying polydimethylsiloxane block length were synthesized from the two classes of oligomers, while controlling the number average molecular weight to approximately 30.0 kg/mole by the addition of 4-t-butylphenol (according to the equations in section 4.3.2).

### 4.1.4 Characterization of Copolymers

The resulting copolymers were analyzed by dynamic thermal gravimetric analysis (TGA), differential scanning calorimetry (DSC), and gel permeation chromatography (GPC) relative to polystyrene standards. The copolymers were also analyzed by $^1$H NMR to determine number average molecular weight ($<M_n>$) and weight percent of polydimethylsiloxane incorporated. The results of the analyses on the series of copolymers are listed in Table 4.1.4.1 and Table 4.1.4.2.
Table 4.1.4.1 Characterization of Polycarbonate - OH-BP-PSX Copolymers

Siloxane Weight %

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<th>Charged (1H NMR)</th>
<th>Obtained (1H NMR)</th>
<th>(&lt;M_n&gt;) (GPC) (kg/mol)</th>
<th>(&lt;M_n&gt;) (GPC) (kg/mol)</th>
<th>(M_w/M_n) (GPC) (kg/mol)</th>
<th>5% Wt loss (°C)</th>
<th>PC Tg (°C)</th>
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Table 4.1.4.2 Characterization of Polycarbonate - OH-P-PSX Copolymers

Siloxane Weight %

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<th>Charged (1H NMR)</th>
<th>Obtained (1H NMR) (kg/mol)</th>
<th>$&lt;M_n&gt;$ (GPC) (kg/mol)</th>
<th>$&lt;M_n&gt;$ (GPC)</th>
<th>$M_W/M_n$</th>
<th>5% Wt loss (°C)</th>
<th>PC Tg (°C)</th>
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<tr>
<td>15</td>
<td>13</td>
<td>33</td>
<td>32.9</td>
<td>2.2</td>
<td>400</td>
<td>146</td>
</tr>
<tr>
<td>30</td>
<td>27</td>
<td>30</td>
<td>31.3</td>
<td>2.0</td>
<td>390</td>
<td>144</td>
</tr>
<tr>
<td>50</td>
<td>47</td>
<td>30</td>
<td>29.9</td>
<td>2.0</td>
<td>415</td>
<td>-----</td>
</tr>
</tbody>
</table>
1H NMR analysis of the copolymers demonstrated that good incorporation of the polydimethylsiloxane oligomers was accomplished, as extraction with hexanes was done before analysis in order to selectively remove any unincorporated polydimethylsiloxane. A representative 1H NMR spectrum is shown in Figure 4.1.4.1. The mole percent incorporation can be determined from the 1H NMR spectra by finding the ratio of the normalized aryl—Si methyl protons at 0.08 ppm relative to the normalized isopropylidene methyl protons at 1.68 ppm. The weight percent incorporation can easily be calculated from this value knowing the formula weight of the two respective repeat units.

Since 4-t-butylyphenol was used to control the molecular weight, <Mn> values could be calculated. Quantitative end capping was assumed and reinforced by the lack of detectable phenol resonances by either 1H NMR or UV-Vis spectroscopy. The relative number average molecular weight of each component could be determined from the ratio of normalized t-butyl proton resonances at 1.32 ppm relative to a particular backbone resonance. The number average molecular weights thus determined for each component could be added along with the molecular weight of the t-butylyphenyl endgroups to determine the <Mn>total values. Alternatively, knowing the mole percent incorporation, the number average molecular weight of the repeat unit (<M0>) could be determined. By determining the value of the normalized isopropylidene methyl proton resonance relative to the normalized t-butyl resonance, the number of these theoretical repeat units could be determined. Multiplying by <M0> and adding the molecular weight of the t-butylyphenyl end groups yields the total number average molecular weight.
Figure 4.1.4.1 $^1$H NMR Spectrum of Polycarbonate-Polydimethylsiloxane Copolymer (400 MHz, CDC$_3$)
The number average molecular weights by GPC and $^1$H NMR are in reasonable agreement as demonstrated in Tables 4.1.4.1 and 4.1.4.2. A number average molecular weight of 30.0 kg/mole is what was projected by utilizing t-butylphenol as the endcapper. One would expect, and it is observed, that the GPC values would be somewhat dependent on copolymer composition since the values are relative to polystyrene standards. All of the copolymers show a monomodal distribution with a polydispersity of around 2.0 as expected for polycondensation.

The values for the glass transition temperature of the polycarbonate phase follow a trend that is dependent on the length of the polydimethylsiloxane oligomer and the amount of polydimethylsiloxane incorporated. The $T_g$ was found to be lower at each composition when smaller polydimethylsiloxane blocks were used. The $T_g$ also was found to decrease substantially more with increasing amount of polydimethylsiloxane for the lower polydimethylsiloxane block lengths. For example, a decrease in the glass transition temperature from 136°C to 119°C was found when increasing the amount of polydimethylsiloxane from 15 to 30 weight percent for an oligomer with a DP = 14. When an oligomer with a DP = 50 was incorporated at the same weight percents, a decrease in the $T_g$ from 143°C to 141°C was observed. A number of different reasons can be cited for these observations. The most obvious is the effect of the smaller average polycarbonate block lengths resulting from the synthesis of the copolymers. This block size decreases with increasing polydimethylsiloxane incorporation. The polycarbonate block size also decreases with decreasing polydimethylsiloxane block size since for a given
composition, the smaller polydimethylsiloxane blocks are more dispersed along the copolymer chain. The smaller polydimethylsiloxane block size also causes an increase in the interfacial area between blocks (ie, more interchange from block to block). The smaller polydimethylsiloxane blocks may also be more soluble in the polycarbonate phase, which could also decrease the Tg.

Previous workers have found the Tg for the polycarbonate phase to decrease depending on the block length of the polydimethylsiloxane. The decrease in Tg has been mostly attributed to the decrease in the polycarbonate block length, but for the copolymers containing smaller polydimethylsiloxane blocks, the decrease has been found to be greater than that which would be expected from this effect alone. The greater ability of the smaller polydimethylsiloxane blocks to mix with the polycarbonate phase has been attributed to the extra decrease in glass transition temperature.

The temperature at which five percent weight loss in an air atmosphere occurs were measured by dynamic TGA. The temperature was observed to decrease with increasing weight percent of polydimethylsiloxane incorporated. An increase in the amount of polydimethylsiloxane incorporated therefore, slightly decreased the thermal stability of the copolymers. The block length of the polydimethylsiloxane did not seem to have an effect on the thermal stabilities. Since the smaller polydimethylsiloxane blocks contain a greater percentage of the Si—aryl functionality, it can be concluded that the thermal stability of the copolymers is dependent on the thermal stability of the polydimethylsiloxane backbone rather than on the functional end groups of the polydimethylsiloxane oligomers.
For comparison, perfectly alternating polydimethylsiloxane-polycarbonate block copolymers of similar compositions were synthesized. The Si—O—C bond containing block copolymers were synthesized by known literature methods from silylamine terminated polydimethylsiloxane oligomers and phenol terminated polycarbonates as discussed in section 3.4.4.1.\textsuperscript{40} The number average molecular weights of the silylamine terminated polydimethylsiloxanes and the phenol terminated polycarbonates were determined by \textsuperscript{1}H NMR and UV-Vis spectroscopy, respectively. A UV-Vis spectrum for a 4.7K polycarbonate oligomer is represented in Figure 4.1.4.2. The perfectly alternating copolymers were synthesized to controlled molecular weights by the addition of 4-\textit{t}-butylphenol. Data for these copolymers is listed in Table 4.1.4.3. The Si—O—C bonds of these copolymers should be more hydrolytically unstable than the Si—aryl bond containing copolymers.
Figure 4.1.4.2 UV-Vis Spectrum of Phenol Terminated Polycarbonate Oligomer
Table 4.1.4.3  Characterization of Perfectly Alternating Block Copolymers

<table>
<thead>
<tr>
<th>&lt;M_n&gt; of PC (kg/mol)</th>
<th>&lt;M_n&gt; of PSX (kg/mol)</th>
<th>Copolymer &lt;M_n&gt; (kg/mol)</th>
<th>PSX in Copolymer (wt. %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GPC</td>
<td>UV-Vis.</td>
<td>1H NMR</td>
<td>GPC</td>
</tr>
<tr>
<td>6.60</td>
<td>4.7</td>
<td>0.88</td>
<td>26.2</td>
</tr>
<tr>
<td>6.60</td>
<td>4.7</td>
<td>2.5</td>
<td>35.6</td>
</tr>
<tr>
<td>—</td>
<td>6.8</td>
<td>0.88</td>
<td>23.3</td>
</tr>
</tbody>
</table>

The hydrolytic stability of the two types of block copolymers was examined by placing samples in a refluxing mixture of THF, chloroform, and water (v: v: v = 70: 20: 10) for a period of time as suggested in a literature reference.\(^{179}\) Two different compositions were analyzed: approximately 15 weight percent polydimethylsiloxane with a DP of 10 -14; approximately 40 - 47 weight percent polydimethylsiloxane with a DP of 29 -35. The samples were analyzed by GPC to determine any decrease in the molecular weight, with the results plotted as percentage of the original <M_n> versus time (Figure 4.1.4.3 and Figure 4.1.4.4).
Figure 4.1.4.3 Relative Molecular Weight Change for Copolymers of Similar Composition Subjected to Conditions of Refluxing THF: Chloroform: Water (v: v: v: = 70: 20: 10) Versus Time
Figure 4.1.4.4 Relative Molecular Weight Change for Copolymers of Similar Composition Subjected to Conditions of Refluxing THF: Chloroform: Water (v: v: v: = 70: 20: 10) Versus Time
Trends can be seen and relative stabilities determined from this data. It can be seen from Figures 4.1.4.3 and 4.1.4.4 that the copolymers containing Si—aryl linkages between blocks are comparatively more hydrolytically stable than the corresponding copolymers which contain Si—O—C bonds. The hydrolytic stability was found to be compositionally dependent, as the polycarbonate segment is degraded under these conditions\textsuperscript{179}. It is assumed that only the polycarbonate segments are degraded in the Si—aryl copolymers. This is reflected in the high stability of the Si—aryl copolymers which contain a high percentage of polydimethylsiloxane.

Comparison with hydrolytically unstable Si—O—C linked random block copolymers (such as those synthesized by General Electric) rather than the perfectly alternating block copolymers would be a better comparison between the two types of materials. The hydrolytic stability of the commercial material was analyzed in ref.\textsuperscript{179} by this method and was found to have a 50 percent lower molecular weight after 480 minutes. Comparison with the Si—aryl bond containing copolymers synthesized here demonstrates a much improved hydrolytic stability for either of the two compositions of Si—aryl bond containing block copolymers.

4.1.5 Conclusions

The synthesis of phenol functionalized polydimethylsiloxanes with Si—aryl bonds was accomplished conveniently through the use of a THP protecting group. The THP group allowed the synthesis of a variety of molecular weights by conventional base catalyzed redistribution reactions, as well as the
regeneration of phenol functionality under mild cleavage conditions. The oligomers were successfully incorporated into bisphenol A polycarbonate, and the resulting copolymers had good melt stability. The hydrolytic stability of the copolymers was found to be superior to other copolymers of similar composition which contained Si—O—C bonds between blocks. These copolymers can therefore be expected to maintain their physical properties in a hydrolytic environment better than the materials currently in use.
4.2 Vinylphenyl Terminated Polycarbonate Oligomers

Polycarbonates which can be subsequently cured into network structures have been synthesized in the past. Many different reactive groups have been incorporated into bisphenol A polycarbonates either along the backbone or at the chain ends and have been reviewed in section 2.1.4. Reactive groups such as diallylbisphenol A, allylphenol, methacrylate, cyanate, benzocyclobutene, and isopropenylphenyl have been investigated as possible curable moieties.

The objective of this research was to synthesize low molecular weight polycarbonate oligomers with styrene-like end groups. This could be accomplished by the addition of vinylphenol to conventional interfacial polycarbonate reactions to form vinylphenylcarbonate terminal groups. The vinylphenyl capped oligomers were expected to react in a similar fashion to styrene, resulting in highly crosslinked network structures.

Unfortunately, 4-vinylphenol is an unstable compound which is known to undergo spontaneous polymerization.\textsuperscript{190-192} The compound is so unstable that uncontrolled polymerization is found to occur in the solid state in the presence of free radical inhibitors.\textsuperscript{192} An alternative source of this simple compound was required for this to be an attractive method of reactive polycarbonate synthesis. Stable precursors to 4-vinylphenol were obtained which could be conveniently hydrolyzed under basic conditions to the phenolate of 4-vinylphenol prior to polymerization.

4.2.1 Synthesis of Oligomers
4-Vinylphenyl carbonate terminated polycarbonate oligomers were synthesized from bisphenol A, phosgene, and 4-vinylphenol as generally demonstrated in Scheme 4.2.1.1.

\[
\begin{align*}
\text{CH}_3\text{C-O-}\text{CH} & \quad \text{KOH} \\
\text{CH}_2 & \quad 35^\circ \text{C}, 30 \text{ min.} \\
\text{K}^+\text{O-CH} & + \text{K}^+\text{O-C-CH}_3
\end{align*}
\]

\[
\begin{align*}
\text{HO-} & \quad \text{triethylamine} \\
\text{O-CH}_2 & \quad \text{H}_2\text{O/CH}_2\text{Cl}_2 \\
\text{COCl}_2 & \quad \text{pH 10.5 - 11.0}
\end{align*}
\]

\[
\begin{align*}
\text{CH}_2 & \quad \text{O-C(} & \quad \text{O-C(} & \quad \text{O-}\text{CH}_2 \\
\text{CH}_2 & \quad \text{)}_n & \quad \text{)} & \quad \text{CH}_2
\end{align*}
\]

Scheme 4.2.1.1 Synthesis of Vinylphenyl Terminated Polycarbonates

The 4-vinylphenol, or more correctly the potassium phenolate of 4-vinylphenol, could be obtained by the facile hydrolytic cleavage of 4-acetoxy styrene\textsuperscript{193} or bis(4-vinylphenyl) carbonate prior to polymerization. The benefit of these compounds is that they are both stable materials which can be purified and stored for extended periods of time, circumventing the problems associated with the instability of 4-vinylphenol. 4-Acetoxy styrene was obtained
from Höchst-Celanese in 96 percent purity, containing 4-acetoxyethylbenzene as impurity. This was not suitable for the synthesis of quantitatively reactive functionalized polycarbonates. 4-Acetoxy styrene was synthesized in high purity and high yields by a modified literature procedure.\textsuperscript{194} Potassium 4-vinylphenolate was synthesized by the literature method and was extracted from the reaction as the aqueous solution. Reaction with acetic anhydride produced the desired compound which was then purified by fractional distillation. Synthesis of bis(4-vinylphenyl) carbonate was also accomplished by reacting the similarly obtained aqueous potassium 4-vinylphenolate with phosgene under interfacial phase transfer catalyzed reaction conditions. The synthesis of both of these compounds is demonstrated in Scheme 4.2.1.2.
Scheme 4.2.1.2 Synthesis of 4-Vinylphenolate Precursors

Each of these compounds could be hydrolyzed under basic conditions to quantitatively yield an aqueous solution of the 4-vinylphenolate as demonstrated in Scheme 4.2.1.1 for 4-acetoxy styrene. The acetate of 4-acetoxy styrene was found to be much more easily cleaved than the aromatic carbonate of the bis(4-vinylphenyl) carbonate. The benefit to using the carbonate is that no reactive byproduct is formed, contrary to the formation of potassium acetate from the cleavage of 4-acetoxy styrene. However, the potassium acetate was found not to interfere in the subsequent polymerization reaction, since it could not form a stable chain end under the basic reaction conditions. The greater ease of cleavage of the 4-acetoxy styrene led to its predominate use as the precursor to vinylphenyl terminated polycarbonate oligomers.

The aqueous solution of potassium 4-vinylphenolate was found to be stable for up to two months at 25°C. After two months of storage with no added inhibitor, approximately one percent of polymerization products were observed by $^1$H NMR. This demonstrates the ability of the potassium salt of 4-vinylphenolate to be stored for extended periods of time prior to use.

Vinylphenyl terminated oligomers of bisphenol A polycarbonate were synthesized to various molecular weights by changing the molar ratio of bisphenol A relative to 4-acetoxy styrene as demonstrated in the following equations:
grams of oligomer desired  

moles of bisphenol A = \[
\frac{\text{grams of oligomer desired}}{((254.29) + (266.30/ \text{DP}))}
\]

moles of 4-acetoxy styrene/2 = \[
\frac{\text{moles of bisphenol A}}{\text{DP}}
\]

In the above equations, the value of 254.29 represents the molecular weight of the bisphenol A polycarbonate repeat unit while the value of 266.30 represents the molecular weight of bis(4-vinylphenyl) carbonate which corresponds to the combined functional chain ends of the resulting reactive oligomer. The DP was determined by dividing the desired molecular weight by 254.29, the molecular weight of the repeat unit.

The functional oligomers were synthesized by two different interfacial methods. Both methods involve the phosgenation of an interfacial mixture of bisphenol A disodium salt, the phenolate of 4-vinylphenol, and phosgene, with a catalytic amount of triethylamine. The two methods differ in the addition of reactants, resulting in a change in mechanism for the overall reaction.

In the first method, an excess of phosgene was introduced into the mixture with all reactants and catalyst present while maintaining the pH between 10 and 11. The samples synthesized by this method were labeled A(<M_n>), where A designates the polymerization method and (<M_n>) designates the projected molecular weight between end groups. This method resulted in close to the expected number average molecular weights (<M_n>), but with broader molecular weight distributions and intrinsic viscosities higher than expected. Quantitative termination was determined by both ^1H NMR and UV-Vis
spectroscopy, each of which detected no phenolic protons to be present. The broad molecular weight distribution was therefore attributed to the formation of terminated oligomers with molecular weights lower than expected, early in the polymerization. The terminated lower molecular weight species are presumably formed preferentially because of a difference in the solubilities of the phenolates in methylene chloride. Since 4-vinylphenol is soluble in methylene chloride while bisphenol A is not, it can be assumed that the phenolate of 4-vinylphenol is more soluble in the methylene chloride layer than is the phenolate of bisphenol A. This difference in phase distribution results in a ratio of phenolate reactants in the methylene chloride layer different from that in the bulk reaction mixture. As the phosgene (which is soluble in the methylene chloride layer) is introduced, reaction with the monofunctional material can preferentially occur leading to low molecular weight terminated oligomers. With a smaller amount of the unreacted monofunctional reactant remaining, higher molecular weight terminated oligomers are now formed.

This distribution of reactants was examined by $^1$H NMR study of the organic layer of an interfacial polymerization mixture at different pH values (Table 4.2.1.1). The total molar ratio of bisphenol A relative to vinylphenol was 5.15:1. When the pH of the aqueous layer was 11.6, similar to the initial pH value of the polymerization conditions, the average molar ratio of bisphenol A units relative to vinylphenol in the organic layer was measured to be 0.58:1. This would yield an average number of 1.2 bisphenol A groups incorporated between end groups, based on the assumption that polymerization could take place preferentially in the organic layer.
Table 4.2.1.1 Effect of pH on Molar Ratio of Reactants in Organic Layer

<table>
<thead>
<tr>
<th>pH</th>
<th>Molar ratio of bisphenol A: vinylphenol</th>
<th>Expected DP</th>
</tr>
</thead>
<tbody>
<tr>
<td>11.0</td>
<td>1.0 : 1</td>
<td>2.0</td>
</tr>
<tr>
<td>11.6</td>
<td>0.58 : 1</td>
<td>1.2</td>
</tr>
<tr>
<td>12.0</td>
<td>0.24 : 1</td>
<td>0.48</td>
</tr>
</tbody>
</table>

total bisphenol A : 4-vinylphenol = 5.15 : 1

This is apparently not as much of a problem when synthesizing high molecular weight polymers because of the smaller amount of monofunctional compound present in the reaction mixture.

Another variable which was found to affect the molecular weight distribution is that of the catalyst concentration. Increasing amounts of catalyst were found to increase the polydispersity by changing the level of low molecular weight oligomers. Since the samples with a higher fraction of low molecular weight material display a greater solution viscosity and overall molecular weight by GPC, the low molecular weight fraction is not considered to be cyclic material. This effect may be related to the phase distribution of reactants, as discussed above. With a higher concentration of catalyst in the organic phase, preferential reaction of the greater amount of monofunctional material present may take place. Table 4.2.1.2 lists the intrinsic viscosities versus the mole percent of triethylamine catalyst for the products of a reaction attempting to synthesize a 5000 g/mole oligomer terminated with 4-t-butylphenol. The GPC traces for these reactions are compared in Figure 4.2.1.1.
**Table 4.2.1.2** Effect of Triethylamine Concentration on Intrinsic Viscosity

<table>
<thead>
<tr>
<th>Triethylamine (mole %) (based on moles of bisphenol A)</th>
<th>Intrinsic Viscosity (dl/g) 25°C; chloroform</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>0.27</td>
</tr>
<tr>
<td>1.0</td>
<td>0.31</td>
</tr>
<tr>
<td>5.0</td>
<td>0.49</td>
</tr>
</tbody>
</table>
Figure 4.2.1.1 GPC Traces Demonstrating the Effect of Catalyst Level on the Formation of Terminated Polycarbonate Oligomers
In order to obtain a more narrow molecular weight distribution, polymerization was accomplished in a two step procedure, whereby low molecular weight chloroformate terminated oligomers were first synthesized in the absence of catalyst and subsequently hydrolyzed and condensed following addition of triethylamine. It is noted in the literature that such a process yields polymers with lower polydispersities.\textsuperscript{31} Phosgene was introduced in the absence of both the triethylamine catalyst and the potassium 4-vinylphenolate, producing low molecular weight chloroformate terminated oligomers with a very narrow molecular weight distribution as demonstrated by the GPC trace of the chloroformate terminated oligomers shown in Figure 4.2.1.2. Addition of the potassium 4-vinylphenolate and triethylamine catalyst resulted in the hydrolysis and condensation to form capped oligomers of the desired molecular weight having low polydispersities. Additional phosgene was introduced in order to insure complete condensation. Oligomers synthesized by this method were labeled B(<M_n>).

As a control, polycarbonate oligomers with nonreactive functional end groups were synthesized to similar molecular weights by similar methods. 4-t-Butylphenol was substituted for the hydrolysis products of 4-acetoxy styrene to synthesize 4-t-butylphenyl carbonate terminated oligomers. These oligomers were designated t-B(<M_n>) and characterized along with the reactive oligomers for comparison.
Figure 4.2.1.2 GPC Trace of Chloroformate Terminated Polycarbonate Oligomer Synthesized Without Catalyst
4.2.2 Synthesis of Crosslinked Polycarbonate Networks

Crosslinked polycarbonate networks could be obtained from the vinylphenyl terminated oligomers. The formation of the crosslinked networks could be effected through a thermally initiated cure reaction of the styrene-like end groups. The mechanism of the thermal initiation was considered to be similar to the thermal self initiation of styrene. This mechanism of styrene initiation has been widely debated, but never-the-less results in the formation of free radicals which initiate the polymerization of the remaining styrene monomer. In the case of the end functionalized polycarbonate oligomers, free radical generation causes initiation of the styrene-like endgroups. In order to obtain the largest processing window possible, free radical initiators were not added to the reactive oligomers.

Propagation is undoubtedly limited by the viscosity increase which is encountered during the formation of the crosslinked network, as well as by the steric requirements of linking multiple oligomers. For this reason, it is expected that the oligomerization of the end groups should not continue beyond a few repeat units.

Partially or totally insoluble crosslinked networks were observed after thermal treatment. The reactive oligomers could be cast from solution and subsequently heated to 200°C to 300°C under vacuum in order to effect a thermal cure. After this thermal treatment, the samples were found to be insoluble. Since the low molecular weight oligomers were also found to flow at relatively low temperatures relative to the temperature of the cure reaction, specimens with a variety of sample geometries could be formed by
compression molding. Reactions were done at different temperatures for varying amounts of time in order to determine the effect on the formation of a three dimensional network.

4.2.2 Characterization of Vinylphenyl Terminated Polycarbonate Oligomers and the Corresponding Networks

4.2.2.1 Molecular Weight of Polycarbonate Oligomers

The molecular weights of the oligomers synthesized by the two different methods were characterized by GPC, intrinsic viscosity (IV), and \(^1\)H NMR. A \(^1\)H NMR spectrum for a projected 2.5 kg/mole oligomer is depicted in Figure 4.2.2.1.1. The \(<M_n>\) obtained for the oligomers by \(^1\)H NMR corresponded reasonably well with that which was predicted from stoichiometry for both synthetic methods. The average number of bisphenol A repeat units between end groups was obtained from the \(^1\)H NMR spectra by finding the ratio of the normalized vinyl proton resonances to that of the normalized isopropylidene proton resonances. Normalization was accomplished by dividing by the number of respective protons for that resonance. The integrated values for the vinyl protons at 5.22 ppm divided by 2 were ratioed to the integration values for the isopropylidene methyl protons at 1.68 ppm divided by 6. Multiplying by 254.29 g/mol, the molecular weight of the polycarbonate repeat unit, gave the \(<M_n>\) between end groups. The total \(<M_n>\) was determined by adding 266.30g/mol. Similarly the \(<M_n>\) for t-butylphenyl terminated polycarbonates could be found by replacing the value of the integrated vinyl protons with those of the normalized (18 t-butyl protons) t-butyl protons at 1.32 ppm.
Figure 4.2.2.1.1 $^1$H NMR Spectrum of 2.5 kg/mol Vinylphenyl Terminated Polycarbonate Oligomer
The values for the $<M_n>$ obtained by GPC relative to polystyrene standards also agree very well with the theoretical values and those obtained by $^1$H NMR for both methods of oligomer synthesis. Although the $<M_n>$ values were found to be similar between the two methods, the polydispersities were found to be different. The pre-phosgenation route to initially form chloroformate terminated oligomers, resulted in vinylphenyl terminated oligomers with lower polydispersities. The intrinsic viscosities were also lower for the oligomers produced by this chloroformate route, reflecting the more narrow molecular weight distribution. The molecular weights and intrinsic viscosities of the oligomers relative to the synthetic route and method of characterization are listed in Table 4.2.2.1.1. The projected $<M_n>$ values were calculated for the $<M_n>$ between end groups while the characterization methods take into account the total molecular weight. The projected $<M_n>$ values are used to designate each sample.
Table 4.2.2.1.1 Molecular Weight Characterization of Oligomers

<table>
<thead>
<tr>
<th>Sample (projected $&lt;M_n&gt;$)</th>
<th>$&lt;M_n&gt;$ (1H NMR) (kg/mol)</th>
<th>IV (25°C; CHCl₃) (dl/g)</th>
<th>$&lt;M_n&gt;$ (GPC) (kg/mol)</th>
<th>$&lt;M_W&gt;/&lt;M_n&gt;$ (GPC)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conventional Synthesis (A)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>A(2.5)</td>
<td>3.0</td>
<td>0.20</td>
<td>2800</td>
<td>5.2</td>
</tr>
<tr>
<td>A(5K)</td>
<td>5.4</td>
<td>0.30</td>
<td>4700</td>
<td>6.0</td>
</tr>
<tr>
<td>A(7.5K)</td>
<td>7.6</td>
<td>0.43</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>A(10K)</td>
<td>10.5</td>
<td>0.70</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Chloroformate Route (B)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>B(1.5K)</td>
<td>1.8</td>
<td>0.10</td>
<td>1300</td>
<td>1.8</td>
</tr>
<tr>
<td>B(2.5K)</td>
<td>3.0</td>
<td>0.21</td>
<td>3600</td>
<td>3.7</td>
</tr>
<tr>
<td>B(5K)</td>
<td>5.3</td>
<td>0.27</td>
<td>6500</td>
<td>3.2</td>
</tr>
<tr>
<td>B(7.5K)</td>
<td>7.0</td>
<td>0.39</td>
<td>8800</td>
<td>4.5</td>
</tr>
</tbody>
</table>

The participation of the potassium acetate (produced during the hydrolysis of the 4-acetoxy styrene) was examined. It is possible for the acetate to be incorporated into the polycarbonate as a mixed carboxylic-carbonic anhydride or as an ester. Under anhydrous conditions, it is known for mixed anhydrides to form. The mixed anhydrides formed under anhydrous conditions are thermally unstable and decompose to the esters at room temperature. Under interfacial polycarbonate reaction conditions with a quaternary ammonium phase transfer catalyst, aliphatic aromatic esters can be formed while no mixed anhydrides could be detected in the final product.
The formation of oligomers which by GPC correspond well to the theoretical number average molecular weights, is one indication that no acetate endgroups are formed. The intrinsic viscosities and the GPC number average molecular weights for the \textit{t}-butyl\textit{p}-phenyl terminated oligomers are also similar. Furthermore, no resonances attributable to the acetate could be detected in the $^1$H NMR. From these indications, it can be concluded that no methyl ester is formed under the reaction conditions. If mixed anhydride is formed during the reaction, it is unstable and displaced by phenolate or hydroxide before completion.

4.2.2.2 Thermal Properties

The thermal properties of the reactive and non-reactive oligomers were charaterized by DSC. This technique was used to characterize the cure temperature, the heat of reaction, and the glass transition temperatures ($T_g$). Multiple scans were required with a quench to room temperature in between scans in order to obtain the $T_g$'s before and after cure. The data is compiled in Table 4.2.2.2.1 with respect to $<M_n>$ of the oligomers, while typical DSC scans obtained from the first and second heat of a $<M_n> = 2.5$ kg/mole reactive oligomer are depicted in Figure 4.2.2.2.1 and Figure 4.2.2.2.2, respectively.
Table 4.2.2.2.1 Characterization of Oligomers by DSC

<table>
<thead>
<tr>
<th>Sample (=&lt;M_n&gt;)</th>
<th>T_g 1st Heat DSC (°C)</th>
<th>T_g 2nd Heat DSC (°C)</th>
<th>Sample (=&lt;M_n&gt;)</th>
<th>T_g 1st Heat DSC (°C)</th>
<th>T_g 2nd Heat DSC (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>B(1.5K)</td>
<td>85</td>
<td>177</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>A(2.5K)</td>
<td>105</td>
<td>155</td>
<td>2.5K</td>
<td>111</td>
<td>111</td>
</tr>
<tr>
<td>A(5K)</td>
<td>126</td>
<td>152</td>
<td>5K</td>
<td>132</td>
<td>132</td>
</tr>
<tr>
<td>A(7.5K)</td>
<td>137</td>
<td>152</td>
<td>7.5K</td>
<td>139</td>
<td>138</td>
</tr>
<tr>
<td>A(10K)</td>
<td>140</td>
<td>150</td>
<td>10K</td>
<td>142</td>
<td>143</td>
</tr>
</tbody>
</table>

First heat to 350°C at 10°C/min. Second heat to 350°C at 10°C/min.
Figure 4.2.2.2.2 DSC Trace of 2.5K Vinylphenyl Terminated Polycarbonate Oligomer (Second Heat at 10°C/min. After First Heat to 350°C at 10°C/min.)
The Tg's obtained on the first heat reflect the low molecular weight of the samples. The Tg's are observed to increase with molecular weight, approaching 150°C, the value for high molecular weight polycarbonate. The exothermic cure reaction of the vinylphenyl end groups can be detected on the first heat above the Tg of the oligomers. The start of the exotherm as well as the range was found to vary with the molecular weight of the oligomers (Table 4.2.2.2.2), as the exotherm began at higher temperatures for higher molecular weight samples. The heat of the exotherm could also be measured and was found to increase with the molar amount of reactive end group (i.e. with a decrease in molecular weight) as expected.

Table 4.2.2.2.2  Heat of Cure Reaction

<table>
<thead>
<tr>
<th>Sample ( (&lt;M_n&gt;) )</th>
<th>(-\Delta H ) (J/g)</th>
<th>Range of Exotherm ( (^\circ C) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bis(4-vinylphenyl) carbonate</td>
<td>107.8</td>
<td>90-200</td>
</tr>
<tr>
<td>B(1.5K)</td>
<td>30.8</td>
<td>114-208</td>
</tr>
<tr>
<td>A(2.5K)</td>
<td>24.2</td>
<td>129-226</td>
</tr>
<tr>
<td>A(5K)</td>
<td>8.7</td>
<td>151-233</td>
</tr>
<tr>
<td>A(7.5K)</td>
<td>3.6</td>
<td>161-208</td>
</tr>
<tr>
<td>A(10K)</td>
<td>1.9</td>
<td>161-234</td>
</tr>
</tbody>
</table>

Scanning a second time after quench cooling from a temperature above the end of the cure exotherm produced a DSC scan which showed an increased Tg from that of the low molecular weight oligomers. For the higher molecular weight oligomers, the Tg increased to 150°C upon cure. The increase in Tg
was even more pronounced for the low molecular weight reactive oligomers, exceeding the value obtained for linear polycarbonate. This reflects the more highly crosslinked network derived from the lower molecular weight oligomers.

In comparison, the nonreactive t-butylphenyl terminated oligomers showed no change in \( T_g \) during the second scan as demonstrated in Table 4.2.2.2.1.

Dynamic thermogravimetric analysis (TGA) was performed on the reactive oligomers. The material was scanned from 30°C to 800°C at 10°C per minute under an air atmosphere in order to determine the thermooxidative stabilities (Figure 4.2.2.2.3). The samples undoubtedly undergo a cure reaction during the course of the analysis, resulting in networks with styrene-like aliphatic linkages at the crosslink points. These linkages do not decrease the thermal stabilities of the resulting networks. In fact, the lower molecular weight oligomers (which result in a higher concentration of these linkages) yield networks which begin to lose volatiles at a higher temperature. This apparently greater thermooxidative stability is a reflection of the more highly crosslinked samples and the possibly slowed oxygen diffusion within the networks.

The residual material remaining at elevated temperatures (char yield) is also observed to be greater for the crosslinked samples than for linear polycarbonates. This is one possible indication that these materials may be more fire resistant than commercial linear polycarbonates. Qualitatively, it is observed that these crosslinked samples do have a reduced tendency to continue burning. Samples were placed in a Bunsen burner flame until ignited, and upon removal from the flame self extinguished in less than 1 second. Furthermore, the samples did not have a tendency to drip when continuing to burn within the Bunsen burner flame.
Figure 4.2.2.2.3 Thermogravimetric Analysis of Reactively Terminated Polycarbonate Oligomers: A(2.5K, 5K, 7.5K, 10K) (Air Atmosphere, 10°C/minute)
4.2.2.3 FTIR Analysis

The cure reaction could also be followed by FTIR spectroscopy. The FTIR spectrum for a \( <M_n> = 2.5 \text{ kg/mole} \) sample is depicted in Figure 4.2.2.3.1. Peaks which are of particular importance are the C=O band at 1775 cm\(^{-1}\), the C—O band at 1229 cm\(^{-1}\), and the peaks which were found to be related to the vinyl end groups at 911 cm\(^{-1}\) and 733 cm\(^{-1}\).

The sample was subjected to a thermal cure under nitrogen by ramping to 300\(^\circ\)C over 1.5 hours followed by holding at this temperature for 1 hour. Analysis of the sample by FTIR spectroscopy after this thermal treatment showed the disappearance of the two peaks attributed to the vinyl end group. The subtraction spectrum is shown along with the cured and initial samples in Figure 4.2.2.3.2.
Figure 4.2.2.3.1 FTIR Spectrum of 2.5K Vinylphenyl Terminated Polycarbonate Oligomer (Polymer Film Cast from Chloroform Solution on a Silicon Wafer)
Figure 4.2.2.3.2 FTIR Spectrum of 2.5K Vinylphenyl Terminated Polycarbonate Oligomer (A) Before; (B) After Thermal Treatment at 300ºC and (C) Subtraction Spectrum (Cast from Chloroform Solution on a Silicon Wafer)
4.2.2.4 Curing of Samples

The curing reaction was examined by subjecting the different samples to different time/temperature profiles. Initial samples were held at 220°C for times ranging from 30 minutes to 2 hours. The samples with different initial molecular weights were examined by soxhlet extraction to determine how the molecular weight of the oligomers affects the extent of the cure reaction or the time required to cure the samples (Table 4.2.2.4.1). From the data, it can be seen that the lower molecular weight oligomers require less time to become 100 percent insoluble. The higher molecular weight oligomers require more time at this temperature, but do become 100 percent insoluble by the end of 2 hours.

Table 4.2.2.4.1 Effect of Cure Time on Sol Fraction

<table>
<thead>
<tr>
<th>Sample</th>
<th>30 minutes*</th>
<th>60 minutes*</th>
<th>90 minutes*</th>
<th>120 minutes*</th>
</tr>
</thead>
<tbody>
<tr>
<td>(&lt;Mₙ&gt;)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>A(2.5K)</td>
<td>0.5%</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>A(5K)</td>
<td>12%</td>
<td>6%</td>
<td>4%</td>
<td>2%</td>
</tr>
<tr>
<td>A(7.5K)</td>
<td>14%</td>
<td>13%</td>
<td>2%</td>
<td>1%</td>
</tr>
<tr>
<td>A(10K)</td>
<td>26%</td>
<td>15%</td>
<td>11%</td>
<td>1%</td>
</tr>
</tbody>
</table>

*Cure Time at 220°C
Samples were also analyzed by soxhlet extraction after curing at 300°C for 40 minutes. A similar trend could be observed at this temperature, where the higher molecular weight samples did not become 100 percent insoluble after this reaction time (Table 4.2.2.4.2).

Table 4.2.2.4.2 Percent Extractable Material After Cure at 300°C for 40 Minutes

<table>
<thead>
<tr>
<th>B(1.2K)</th>
<th>B(2.5K)</th>
<th>B(5K)</th>
<th>B(7.5K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2%</td>
<td>3%</td>
<td>14%</td>
<td>22%</td>
</tr>
</tbody>
</table>

The soluble portion extracted from the cured B(5K) oligomer was analyzed by GPC and by \(^1\)H NMR to determine how much reaction had taken place. GPC analysis determined that the molecular weight was similar to that of the initial uncured oligomer. \(^1\)H NMR on the other hand, indicated a lower concentration of vinyl end groups present in the sample. This may indicate that some nonreactive end groups are present in this sample, or that termination of the reactive end groups occurred before propagation could take place. The latter explanation is backed up by the observance of new peaks in the \(^1\)H NMR spectrum as well. The fact that some vinylphenyl end groups remain also indicates that the reaction time was not sufficient to complete the cure; although, this is only speculation and further research would be required to ascertain the reaction progress.
4.2.2.5 Fracture Toughness

Fracture toughness was determined by single edge notched bending ($K_{1c}$) according to ASTM D-5045-91 (E-399-90) for samples cured at 220°C for 30 minutes and for samples cured at 300°C for 40 minutes. Linear polycarbonate samples (similar to the molecular weights of the reactive oligomers before cure, as well as commercial material) were also tested for comparison. The fracture toughness data is compiled in Table 4.2.2.5.1.

Table 4.2.2.5.1 $K_{1c}$ Fracture Toughness Values

<table>
<thead>
<tr>
<th>Cured at 220°C/30min.</th>
<th>Cured at 300°C/40min.</th>
<th>Non-reactively Terminated</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample (&lt;$M_n$&gt;)</td>
<td>$K_{1c}$ Fracture Toughness (MPa•m$^{1/2}$)</td>
<td>Sample (&lt;$M_n$&gt;)</td>
</tr>
<tr>
<td>A(1.2K)</td>
<td>—</td>
<td>B(1.2K)</td>
</tr>
<tr>
<td>A(2.5K)</td>
<td>—</td>
<td>B(2.5K)</td>
</tr>
<tr>
<td>A(5K)</td>
<td>3.09 ± 0.23</td>
<td>B(5K)</td>
</tr>
<tr>
<td>A(7.5K)</td>
<td>3.31 ± 0.27</td>
<td>B(7.5K)</td>
</tr>
<tr>
<td>A(10K)</td>
<td>3.46 ± 0.19</td>
<td>B(10K)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Lexan 150</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Calibre 300-3</td>
</tr>
</tbody>
</table>

The $K_{1c}$ fracture toughness shows that the cured samples retain some of the inherent toughness properties of high molecular weight linear...
polycarbonate. However, the toughness of the networks was found to decrease with a decrease in the initial oligomer molecular weights. The lower molecular weight between crosslinks obtained from these lower molecular weight oligomers is not able to absorb the energy as well as the higher molecular weights between crosslinks. It further appears that to a first approximation, the fracture toughness of the network material corresponds closely to that of the low molecular weight t-butylphenyl terminated oligomers; although the effect of residual linear material not incorporated into the network structure cannot be ignored in these results.

4.2.2.6 Dynamic Mechanical Analysis

The dynamic mechanical spectra of the uncured, semi-cured, and fully cured samples were examined to determine if a shift in the secondary relaxations could be detected, and how this might correlate to the fracture toughness values. Samples were analyzed at a frequency of 1 Hertz in three point bending mode and the tan δ peak was plotted versus temperature for samples with different cure histories. Vinylphenyl terminated oligomers B(5K) and B(7.5K) were of sufficient molecular weight to form three point bending samples by compression molding. Uncured oligomers of lower molecular weight could not be measured as they did not have sufficient molecular weight to form suitable samples. To determine the DMA spectrum of fully cured networks of these samples, the compression molded oligomers were cured in an oven under nitrogen atmosphere at 250°C for 3 hours (soxhlet extraction of these samples yielded 100 percent insoluble materials). DSC was also performed on these cured samples and showed an increase in the Tg from that
of the second heat of the dynamically scanned samples in Table 4.2.2.2.1. The
cured B(5K) sample showed a $T_g$ of 162°C, while the cured B(7.5K) sample
showed a $T_g$ of 160°C, indicative of the more fully cured networks.

DMA spectra of uncured B(5K), B(5K) cured at 300°C for 40 minutes, and
B(5K) cured at 250°C for 3 hours are depicted in Figure 4.2.2.6.1, while the
DMA spectra of similar samples of B(7.5K) are depicted in Figure 4.2.2.6.2. The
DMA spectrum for linear Dow Calibre-300-3 polycarbonate is represented in
Figure 4.2.2.6.3 for comparison.
Scan in 3 Point Bending
Dynamic Stress: 1.64e+06Pa
Static Stress: 1.96e+06Pa
Frequency: 1.00 Hz

Figure 4.2.2.6.1 DMA Spectra for B(5K) A) Uncured Oligomer; B) Cured at 300°C for 40 Minutes; C) Cured at 250°C for 3 Hours
Figure 4.2.2.5.2  DMA Spectra for B(7.5K) A) Uncured Oligomer; B) Cured at 300°C for 40 Minutes; C) Cured at 250°C for 3 Hours
Figure 4.2.2.6.3 DMA Spectrum for Dow Calibre 300-3 Linear Polycarbonate
From these figures it can be seen that the peak due to the glass transition shifts to higher temperatures with the extent of cure. Furthermore, the low temperature relaxation peak changes with network formation. The 5K samples represents this change as the cure causes a broadening of the low temperature peak toward higher temperatures. The same effect can be seen in the 7.5K sample, but to a lower extent than in the 5K sample.

4.2.2.7 Tensile Properties

The tensile mechanical properties were determined from stress-strain analysis of cured samples and nonreactive oligomers. The data obtained for these samples is contained in Table 4.2.2.7. Again, for the network materials the testing was done on samples which were not completely cured in all cases.
### Table 4.2.2.7 Tensile Mechanical Properties

<table>
<thead>
<tr>
<th>Sample ($&lt;M_n&gt;$)</th>
<th>Tensile Strength (MPa)</th>
<th>Tensile Modulus (GPa)</th>
<th>Tensile Elongation (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>B(1.5K)**</td>
<td>86.3</td>
<td>2.6</td>
<td>7.5</td>
</tr>
<tr>
<td>B(2.5K)**</td>
<td>96.7</td>
<td>2.7</td>
<td>$&gt;30^{**}$</td>
</tr>
<tr>
<td>B(5K)**</td>
<td>82.1</td>
<td>3.2</td>
<td>$&gt;30^{**}$</td>
</tr>
<tr>
<td>A(7.5K)*</td>
<td>78.6</td>
<td>2.7</td>
<td>$&gt;30^{**}$</td>
</tr>
<tr>
<td>A(10K)*</td>
<td>75.2</td>
<td>2.8</td>
<td>$&gt;30^{**}$</td>
</tr>
</tbody>
</table>

**Non-reactively Terminated Oligomers**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Tensile Strength (MPa)</th>
<th>Tensile Modulus (GPa)</th>
<th>Tensile Elongation (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>t-B(2.5K)</td>
<td>73.5</td>
<td>2.8</td>
<td>3.2</td>
</tr>
<tr>
<td>t-B(5K)</td>
<td>74.7</td>
<td>2.9</td>
<td>4.9</td>
</tr>
<tr>
<td>t-B(7.5K)</td>
<td>77.6</td>
<td>2.9</td>
<td>$&gt;30^{**}$</td>
</tr>
<tr>
<td>t-B(10K)</td>
<td>77.1</td>
<td>2.8</td>
<td>$&gt;30^{**}$</td>
</tr>
</tbody>
</table>

*Cured at 220°C for 30 minutes; **Cured at 300°C for 40 minutes; ***Not broken due to limit of extensometer

#### 4.2.2.8 Scanning Electron Microscopy (SEM)

Polycarbonates are known to crystallize when stressed samples are exposed to acetone. The effect that network formation has on the ability of the polycarbonate to crystallize when exposed to solvent was investigated. Fractured $K_{1C}$ sample bars were placed in acetone for 1, 30, and 120 minutes to determine how this solvent exposure affected the fracture surface. The fracture surfaces of a polycarbonate control (exposed to acetone for 1, 30, and 60 seconds) and of samples cured at 300°C for 40 minutes were analyzed by SEM to examine the morphology that developed. The scanning electron
micrographs with 2000 X magnification are shown in Figures 4.2.2.8.1 through 4.2.2.8.5.

The micrographs demonstrate the development of crystallinity with exposure time. While the linear polycarbonate control develops crystallinity immediately (requiring a different time scale to demonstrate the immediate crystallization), the cured samples show a decreased tendency towards crystallization. The only sample in which no crystallinity can be detected to develop on the observed time scale is the cured B(1.5K) material. Although the micrographs do show some surface characteristics for this sample, it is believed to be either air bubbles or possibly demonstrates the extraction of low molecular weight uncured material.
Figure 4.2.2.8.1 SEM of Polycarbonate (Calibre 300-3) Fracture Surface After Acetone Exposure

Acetone Exposure: 1 second

Acetone Exposure: 30 seconds

Acetone Exposure: 60 seconds
Figure 4.2.2.8.2  SEM of B(1.5K) Cured at 300°C for 40 Minutes Fracture Surface After Acetone Exposure
Figure 4.2.2.8.3 SEM of B(2.5K) Cured at 300°C for 40 Minutes Fracture Surface After Acetone Exposure
Figure 4.2.2.8.4 SEM of B(5K) Cured at 300°C for 40 Minutes Fracture Surface After Acetone Exposure
Figure 4.2.2.8.5 SEM of B(7.5K) Cured at 300°C for 40 Minutes Fracture Surface After Acetone Exposure

Acetone Exposure: 120 minutes
Acetone Exposure: 30 minutes
Acetone Exposure: 1 minute
The amount of crystallinity is observed to increase with the expected increase in molecular weight between crosslinks; although, these samples also have a greater amount of residual uncured material. Although from this data it is difficult to ascertain whether the observed increase in crystallinity with initial oligomer molecular weight is due entirely to the residual uncured material or because of the higher molecular weight between crosslinks, it is postulated that some of the crystallinity is developed in the crosslinked network itself and not entirely from the soluble portion. Evidence of this is demonstrated by the fact that the cured B(1.5K) and B(2.5K) samples have similar percentages of residual insoluble portions (2% and 3%, respectively) determined from soxhlet extraction data; yet the cured B(1.5K) sample develops no crystallinity while the cured B(2.5K) sample does crystallize slowly.

4.2.2.9 Adhesion Properties

A cursory investigation of the adhesion properties of these new materials to aluminum was performed by single lap shear tests (Table 4.2.2.9.1). Aluminum coupons were prepared according to ASTM standard methods.
<table>
<thead>
<tr>
<th>Reactively Terminated</th>
<th>Non-Reactively Terminated</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oligomers Cured at 220°C for 30 minutes</td>
<td>Polycarbonates</td>
</tr>
<tr>
<td>Sample $&lt;M_n&gt;$</td>
<td>Single Lap Shear Strength (PSI)</td>
</tr>
<tr>
<td>A(2.5K)</td>
<td>4890 ± 140</td>
</tr>
<tr>
<td>A(5K)</td>
<td>5920 ± 360</td>
</tr>
<tr>
<td>A(10K)</td>
<td>5500 ± 300</td>
</tr>
<tr>
<td>Lexan 150</td>
<td>3550 ± 360</td>
</tr>
</tbody>
</table>

It can be seen that the materials do have a potential for use as structural adhesives. Compared with commercial polycarbonate, the cured samples show an increased adhesion to this substrate. This is possibly due to the fact that the low molecular weight of the reactive oligomers allows them to flow better than the high molecular weight material, and thus adhere better to the substrate before being cured into a network. Except for very low molecular weight materials (where cohesive failure is observed), the nonreactively terminated oligomers also demonstrate an increase in adhesion to the substrate relative to high molecular weight polycarbonate. Again, this is probably due to the better flow properties of the low molecular weight materials.
4.2.2.10 Formation of Copolymer Networks

The solubility of the reactive oligomers in other vinyl monomers was determined. The oligomers were found to be soluble in styrene, p-methylstyrene, p-t-butylstyrene, styrene/acrylonitrile, and 50:50 mixtures of styrene and unsaturated polyester, in amounts up to 30 weight percent depending on the molecular weight of the oligomer (lower molecular weights were more soluble). Unfortunately, the oligomers were almost completely insoluble in all methacrylates examined.

The solubility of the oligomers in styrene and styrene derivatives allows the formation of crosslinked copolymers, or toughened crosslinked polystyrene networks. Although materials with this type of network structure were synthesized, no characterization was performed on the samples. The volatility of styrene monomer and the equipment available were not conducive to the formation of test samples with the proper geometry for analysis. These materials would lend themselves very well to resin transfer molding applications, and this should be examined in the future.

4.2.3 Conclusions

The synthesis of vinylphenyl terminated polycarbonate oligomers was accomplished by the introduction of the hydrolysis products of 4-acetoxy styrene or bis(4-vinylphenyl) carbonate into a typical interfacial polymerization mixture. The number average molecular weight of the oligomers was controlled by the ratio of reactive monofunctional material to bisphenol A introduced to the reaction. The isolated oligomers were observed to undergo a thermally
induced cure reaction to form insoluble networks. The rate of formation of a totally insoluble network was found to be dependent on the molecular weight of the reactive telechelic oligomers, where the higher molecular weight oligomers cured more slowly. The mechanical properties of the cured materials were examined and found to relate to many of the characteristics of linear high molecular weight polycarbonate, while the solvent resistance of the cured samples was greatly improved over the linear material. Furthermore, these materials show potential for application as structural adhesives.
4.3 Phosphorus Containing Polycarbonates

Bisphenol A polycarbonates are considered to be somewhat fire resistant with a limiting oxygen index of 26 and a classification of V2 (1.6 mm and 3.2 mm) according to UL 94.\textsuperscript{5} Fire regulations, however, have required the development of improved fire resistant polycarbonate materials.\textsuperscript{5} Many different additives have been used to improve upon this property including a number of phosphorus containing materials, since it is well known that phosphorus can improve the fire resistance of a material.\textsuperscript{197} Incorporation of fire retardants into the backbone of the polymer have also been investigated and commercialized.\textsuperscript{5}

The incorporation of phosphorus containing comonomers into the bisphenol polycarbonate backbone has been reviewed in section 2.1.5.2. Most of the research in this area has involved the formation of hydrolytically unstable phosphonate or phosphate groups in the polycarbonate. The purpose of the present work was to investigate the feasibility of incorporating triphenylphosphine oxide derivatives into polycarbonate, and to determine the effect on the fire resistance and other properties. The approach taken was to synthesize a bisphenol and a monophenol (for use as an end group) of triphenylphosphine oxide and incorporate them into bisphenol A polycarbonate by interfacial polymerization. In this way, hydrolytically and thermally stable linkages should result.

4.3.1 Synthesis and Characterization of Phosphorus Containing Polymers
4.3.1.1 Monomer synthesis

Bis(4-hydroxyphenyl)phenylphosphine oxide (triphenylphosphine oxide bisphenol) was synthesized by the reaction of the Grignard reagent of 2-(4-
bromophenoxy)tetrahydropyran with phenyl phosphonic dichloride followed by acid catalyzed cleavage of the tetrahydropyranyl ether (Scheme 4.3.1.1.1). The bisphenol could be obtained in high purity by this method. Alternatively, the similar synthesis utilizing the Grignard reagent obtained from 4-bromoanisole and subsequent acid cleavage of the methyl ether yielded a highly colored product which could not be decolorized.

Scheme 4.3.1.1.1 Synthesis of Bis(4-hydroxyphenyl)phenyphosphine Oxide
A monofunctional phenol derived from triphenylphosphine oxide was also synthesized in order to use as a model compound and to use as an endcapper in the synthesis of polycarbonates. 4-Hydroxyphenyldiphenylphosphine oxide (triphenylphosphine oxide phenol) was synthesized from the reaction of the Grignard reagent obtained from 4-bromoanisole with diphenylphosphinic chloride followed by cleavage of the methyl ether with HBr (Scheme 4.3.1.1.2). This method yielded pure product after recrystallization.

![Chemical structures](image)

**Scheme 4.3.1.1.2** Synthesis of 4-Hydroxyphenyldiphenylphosphine Oxide

### 4.3.1.2 Model Reactions

In order to determine the feasibility of forming polycarbonates from the triphenylphosphine oxide bisphenol, some model reactions were performed. It is known in the literature that tertiary phosphine oxide (or phosphine)
compounds react with phosgene to chlorinate the phosphorus nucleus forming tertiary phosphine dichlorides.\textsuperscript{198} These halogenated compounds are hydrolytically unstable and can be easily hydrolyzed to the tertiary phosphine oxide (Scheme 4.3.1.2.1). This reaction could be competitive with the formation of the polycarbonate during phosgenation; furthermore, the tertiary phosphine halide may cause undesirable side reactions. Model reactions were performed in order to determine to what extent, if any, this might interfere with the polymerization.

![Scheme 4.3.1.2.1 Formation and hydrolysis of Tertiary Phosphine Dichloride](image)

Under the interfacial conditions of the polymerization, the triphenylphosphine dichloride formed from phosgenation should be quickly hydrolyzed back to the phosphine oxide. In order to model these reactions, triphenylphosphine oxide and triphenylphosphine were phosgenated under conditions similar to those of an interfacial polycarbonate polymerization. Under these conditions, only triphenylphosphine oxide could be isolated from the reaction mixture. Although from this experiment it is difficult to determine whether the triphenylphosphine oxide reacted with phosgene, the triphenylphosphine undoubtedly did. Since the triphenylphosphine quantitatively yielded triphenylphosphine oxide, the hydrolysis of the triphenylphosphine
dihalide must take place rapidly under these conditions. It is worth noting that
the reaction with triphenylphosphine oxide was observed to consume
phosgene in a similar fashion to the triphenylphosphine reaction; that is, the
exothermic characteristics of the reaction were qualitatively similar.

Since phosgene can possibly react unfavorably with the phosphine oxide
bisphenol monomer similarly to the triphenylphosphine oxide, it was examined
whether high molecular weight bisphenol A polycarbonate could be formed in
the presence of triphenylphosphine oxide. Interfacial polymerization was
conducted in the presence of a stoichiometric amount of triphenylphosphine
oxide utilizing a slight excess (1.5 equivalents) of phosgene. The
polycarbonate obtained was isolated and examined by intrinsic viscosity and
$^{31}\text{P NMR}$. The intrinsic viscosity in chloroform was determined to 1.45 dl/g,
indicating that high molecular weight polymer was formed. $^{31}\text{P NMR}$ was done
to determine if any of the phosphorus compound was incorporated into the
backbone of the polymer. No phosphorus could be detected.

Although this model polymerization indicates that the reaction of phosgene
with the phenolate of bisphenol A is faster than the reaction with
triphenylphosphine oxide, the reaction of the phenolate of the
triphenylphosphine oxide bisphenol may not be as competitive.

The reaction of the triphenylphosphine oxide bisphenol with phosgene to
form polycarbonate was modeled by the synthesis of bis(triphenylphosphine
oxide) carbonate from 4-hydroxyphenyldiphenylphosphine oxide. The
monophenol was reacted with phosgene under the interfacial polymerization
conditions and isolated from the reaction. The isolated product was examined
by $^{1}\text{H}$ and $^{31}\text{P NMR}$. NMR analysis determined that the expected carbonate
product was synthesized in approximately 98 percent purity with the impurity being residual starting material. This indicates that the reaction to form carbonate is indeed faster than the formation of tertiary phosphorus dichloride compound.

For comparison, bis(4-cumylphenyl) carbonate was synthesized under the same conditions. This compound is formed in quantitative yield with no detectable residual starting material by $^1\text{H}$ NMR. This indicates that the reaction of the triphenylphosphine oxide phenolate with phosgene may not be as fast as the reaction of phosgene with 4-cumylphenolate.

4.3.1.3 Homopolycarbonate Synthesis and Characterization

The synthesis of homopolycarbonate of bis(4-hydroxyphenyl)phenylphosphine oxide was attempted with limited success. Interfacial and solution reactions were attempted, yielding only low molecular weight material in each case.

The synthesis of the homopolycarbonate of bis(4-hydroxyphenyl)phenylphosphine oxide was attempted by interfacial methods, but only low molecular weight material was isolated from the reaction. A large excess of phosgene was used ($>10$ equivalents), but high molecular weights could not be attained during numerous attempts. The material was analyzed by intrinsic viscosity, $^1\text{H}$ and $^{31}\text{P}$ NMR, DSC, and TGA.

The intrinsic viscosities in chloroform at 25°C ranged from 0.14 to 0.18 dl/g for the attempted polymerizations, while the $^1\text{H}$ NMR analysis (Figure 4.3.1.3.1) indicated residual phenol end groups to be present (indicating the low molecular weight of the materials). The $^{31}\text{P}$ NMR spectrum (Figure 4.3.1.3.2),
which should depict a single peak, showed multiple unidentified phosphorus peaks to be present in the samples which could not be explained.

Thermal analysis of the samples by DSC indicated a $T_g$ of 202°C with no detectable $T_m$. Given the low molecular weight of the sample, it is expected that the $T_g$ of high molecular weight polymer would be higher than this value. Thermogravimetric analysis in air demonstrated the decreased thermooxidative stability of this low molecular weight material compared to bisphenol A polycarbonate, but did demonstrate an increase in the char yield at elevated temperature (Figure 4.3.1.3.3).
Figure 4.3.1.3.1 $^1$H NMR Spectrum of Polycarbonate of Bis(4-hydroxyphenyl)phenylphosphine Oxide (400 MHz, CDCl$_3$)
Figure 4.3.1.3.2 $^{31}$P NMR Spectrum of Polycarbonate of Bis(4-hydroxyphenyl)phenyolphosphine Oxide (400 MHz, CDCl$_3$)
Figure 4.3.1.3.3 Thermogravimetric Analysis for Polycarbonate of Bis(4-hydroxyphenyl)phenylphosphine Oxide (Air Atmosphere, 10°C/min.)
An attempt was also made to synthesize the homopolycarbonate by solution polymerization in anhydrous pyridine/methylene chloride. After 1 equivalent of phosgene was added, the reaction mixture formed an insoluble gel. Phosgene addition was continued, but the gel remained. Addition of water to the reaction mixture resulted in dissolution of the previously insoluble material. The product was analyzed by $^{1}$H and $^{31}$P NMR and the same features were present as for the interfacially produced material.

Although the exact nature of the gel was not determined, it is postulated that the tertiary phosphine dihalide is participating in the reaction with the phenol functional groups under the anhydrous conditions. However, the linkages are hydrolytically unstable. High molecular weight material could not be attained because of the difficulty of quantitative reaction within the gel.

4.3.1.4 Synthesis and Characterization of Phosphorus Containing Polyarylate

The polyarylate of the triphenylphosphine oxide bisphenol and terephthaloyl chloride was synthesized by interfacial methods to determine if the monomer was of sufficient purity for the synthesis of high molecular weight material (Scheme 4.3.1.4.1). This reaction was first done with no added monofunctional reagent in order to form uncontrolled molecular weight polymer. A highly viscous solution resulted, and analysis after isolation of the polymer yielded an IV of 0.88 dl/g. A second reaction was performed in which the molecular weight was controlled to form a polymer with expected $<M_n>$ of 40.0 kg/mole by offsetting the stoichiometry and end capping with 4-t-butylphenol. The intrinsic viscosity of this sample was determined to be 0.46 dl/g.
The polyarylate was analyzed by \(^1\text{H}\) and \(^{31}\text{P}\) NMR, DSC, and TGA. The NMR spectra are depicted in Figures 4.3.1.4.1 and 4.3.1.4.2. Thermal analysis of the polymer is tabulated in Table 4.3.1.4.1, while the TGA trace is depicted in Figure 4.3.1.4.3.

It can be seen from this data that the reaction to form the polyarylate of the bisphenol monomer proceeds to high molecular weight with the formation of a polymer with interesting properties. The very high char yield of the polymer is very interesting indeed.

\[
\begin{align*}
\text{Cl-C-} & \quad \text{C-Cl } + \text{ HO-} & \text{P-} & \quad \text{P-OH} \\
\text{+ } & \quad \text{OH} & \text{tetraethylammonium bromide} \\
\text{H}_2\text{O/CH}_2\text{Cl}_2 \\
\text{pH 10.5 - 11.0}
\end{align*}
\]

\[
\begin{align*}
\text{Ph-O-} & \text{(Ph-C-O-Ph-P-O)}_n \\
\text{Ph-O-} & \text{(Ph-C-O-Ph)} \\
\end{align*}
\]

**Scheme 4.3.1.4.1 Synthesis of Phosphorus Containing Polyarylate**
Figure 4.3.1.4.1 $^1$H NMR Spectrum for Polyyarylate of Bis(4-hydroxyphenyl)phenylphosphine Oxide and Terephthaloyl Chloride (400 MHz, CDCl$_3$)
Figure 4.3.1.3.2 $^{31}$P NMR Spectrum for Polyarylate of Bis(4-hydroxyphenyl)phenylphosphine Oxide and Terephthaloyl Chloride (400 MHz, CDCl$_3$)
Figure 4.3.1.3.3 Thermogravimetric Analysis for Polyarylate of Bis(4-hydroxyphenyl)phenylphosphine Oxide and Terephthaloyl Chloride (Air Atmosphere, 10°C/min.)
Table 4.3.1.4.1 Thermal Analysis of Phosphorus Polyarylate

<table>
<thead>
<tr>
<th>Tg (°C)</th>
<th>5% Weight Loss (°C)</th>
<th>Weight at 800°C (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>253</td>
<td>491</td>
<td>48%</td>
</tr>
</tbody>
</table>

4.3.1.5 Synthesis of Polycarbonate Copolymers

The phosphorus containing bisphenol was incorporated into bisphenol A polycarbonate in varying amounts up to 50 weight percent of the repeat unit. Copolymers were synthesized by interfacial techniques with 1, 5, 10, 25, and 50 weight percent of the repeat unit while the molecular weight was controlled by the addition of 4-t-butylphenol to the reaction mixture (Scheme 4.3.1.5.1). Bisphenol A polycarbonates with triphenylphosphine oxide termination were also synthesized by the substitution of 4-hydroxyphenyldiphenylphosphine oxide for 4-t-butylphenol.
Scheme 4.3.1.5.1 Synthesis of Phosphorus Containing Copolymers

4.3.1.6 Characterization of Phosphorus Containing Polycarbonates

The relative molecular weight of the polymers and copolymers were analyzed by intrinsic viscosity and GPC relative to polystyrene standards, while the incorporation was determined by $^1$H NMR (Table 4.3.1.6.1). The molecular weight and end groups were controlled by the addition of a monofunctional phenol, either 4-$t$-butylyphenol or 4-hydroxyphenyldiphenylphosphine oxide. In the synthesis of the copolymers, 2.4 mole percent of 4-$t$-butylyphenol relative to the total bisphenol present was used to control the molecular weight. The
intrinsic viscosity of the copolymers was found to remain constant at this level of monofunctional phenol through the copolymer containing 10 weight percent of comonomer. A decrease in viscosity was observed for the 25 weight percent copolymer, so the amount of added monofunctional reagent was decreased to 1.6 mole percent for the synthesis of the 50/50 copolymer, resulting in an intrinsic viscosity closer to the other materials.

Table 4.3.1.6.1 Characterization of Phosphorus Containing Copolymers

<table>
<thead>
<tr>
<th>Sample</th>
<th>Incorporation ((^{1}\text{H NMR})) (wt. %)</th>
<th>Intrinsic Viscosity ((\text{CHCl}_3; 25^\circ\text{C})) (dl/g)</th>
<th>Tg ((^\circ\text{C}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>1% PPO*</td>
<td>1</td>
<td>0.75</td>
<td>154</td>
</tr>
<tr>
<td>5% PPO*</td>
<td>5</td>
<td>0.75</td>
<td>156</td>
</tr>
<tr>
<td>10% PPO*</td>
<td>9</td>
<td>0.72</td>
<td>159</td>
</tr>
<tr>
<td>25% PPO*</td>
<td>24</td>
<td>0.49</td>
<td>166</td>
</tr>
<tr>
<td>50% PPO**</td>
<td>48</td>
<td>0.69</td>
<td>186</td>
</tr>
</tbody>
</table>

* Molecular weight controlled with 2.6 mole percent 4-t-butylphenol
**Molecular weight controlled with 1.5 mole percent 4-t-butylphenol

Contrary to the homopolymerization, the quantitative incorporation of bis(4-hydroxyphenyl)phenylphosphine oxide as a comonomer into bisphenol A polycarbonates proceeded very well. High molecular weight materials were synthesized as evidenced by the intrinsic viscosity and GPC values.

The Tg's of the copolymers were determined by DSC and are listed in Table 4.3.1.6.1 relative to the percent comonomer. An analysis of the trend in copolymer Tg's by the Fox-Flory equation indicates that the high molecular
weight homopolymer should have a $T_g$ of 224°C, as extrapolated from Figure 4.3.1.6.1.

![Graph showing the relationship between 1/$T_g$ and Wt. % Bisphenol A Polycarbonate.]

**Figure 4.3.1.6.1** Linear Relationship of Copolymer Tg's (Fox-Flory Equation)

Dynamic thermogravimetric analysis (TGA) in an air atmosphere was performed on the samples in order to determine the relative thermooxidative stabilities of the copolymers (Figure 4.3.1.6.2). The residual weight remaining at high temperatures was also observed as an indication of the fire resistance properties of the materials. From the TGA, the copolymers were determined to be stable materials with nominal weight loss before 400°C, and demonstrated
an observable increasing trend in the char yield with increasing phosphorus content. In fact the, the char yield at 700°C increases from 0 percent for commercial polycarbonate to approximately 30 percent for the 50/50 copolymer.
Figure 4.3.1.6.2 Thermogravimetric Analysis for Co-polymerates of Bis(4-hydroxyphenyl)phenylphosphine Oxide and Bisphenol A (Air Atmosphere, 10°C/min.)
The fire resistance of the novel copolymers was further examined by cone calorimetry, the results of which are graphically depicted in Figure 4.3.1.6.3. From the cone calorimetry data which measures the heat release rate with time, a definite improvement can be detected for the copolymers over a bisphenol A polycarbonate control sample. An improvement in the heat release rate is observed with as little as 1 percent of the phosphorus unit incorporated.

The polycarbonate with triphenylphosphine oxide termination was also examined in comparison to the control and copolymer samples. Again, an improvement can be detected with the small amount of triphenyl phosphate oxide introduced at the chain ends of this polymer.
Figure 4.3.1.6.3 Cone Calorimetry Data for Phosphorus Containing Polycarbonates
4.3.2 Conclusions

Homopolycarbonates of the triphenylphosphine oxide bisphenol could not be synthesized to high molecular weight under the conditions examined, although the synthesis of a series of copolycarbonates of bis(4-hydroxyphenyl)phenylphosphine oxide and bisphenol A was accomplished. The copolymers were found to have high char yields and qualitatively examined fire extinguishing capabilities. Along with the observance of decreased heat release rates as measured by cone calorimetry, these materials show a potential for use as flame retardant materials.
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6.0 VITA

Daniel Michael Knauss was born in Allentown, Pennsylvania on January 16, 1967. He graduated from Brandywine Heights Area High School as Valedictorian in 1985. He then entered the Polymer Science Program at The Pennsylvania State University and participated in a co-operative education program which involved research at GE Plastics and IBM Almaden Research Center. He graduated with a B.S. in May, 1990 and entered the graduate program in chemistry at Virginia Polytechnic Institute and State University in August, 1990. Under the direction of Professor James E. McGrath, Dan performed his dissertation research in the area of polycarbonate synthesis and characterization. He received his Ph.D. in Chemistry in September, 1994. Immediate plans for Dan include a post-doctoral position at École Polytechnique Fédérale de Lausanne in Lausanne, Switzerland. Dan intends to obtain a faculty position at a research institution following this post-doctoral experience.

Daniel M. Knauss