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Sustainable Polycarbonate Nanocomposites: Impact of Production Method and Composition

by

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Submitted to the Graduate Faculty as partial fulfillment of the requirements for the

Doctor of Philosophy Degree in

Engineering

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An Abstract of

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The overall goal of this research is to apply the principle of green engineering to produce bio-sourced polycarbonate (PC) based composites with properties similar to BPA-PC. To synthesize PC in a more sustainable way, transesterification polymerization with diphenyl carbonate (DPC) was chosen as the production method. The bio-derived monomer, isosorbide, was chosen as the alternative monomer to the traditional petroleum monomer biphenyl-A (BPA). Alumina-polycarbonate (AL-PC) nanocomposites were produced through melt phase in-situ polymerization to improve mechanical and thermal properties.

The first focus of this study was to produce nanocomposites of BPA-PC and ALNW using in-situ melt phase polymerization. The result will be compared to those from an earlier study using solution based polymerization.

Alumina nanowhiskers (ALNW) were used to synthesize AL-PC nanocomposites using melt phase polymerization, because the hydroxyl groups on the ALNW surface can react with DPC during polymerization. The presence of bonded BPA-PC on the ALNW surface was confirmed following in-situ polymerization. Molecular weight of PC
produced are calculated using NMR end group analysis. The effect of solid state polymerization at gradually increased temperature is reported. Heat resistance and mechanical properties of BPA-PC and AL-BPA nanocomposites were compared and evaluated.

Copolymer of isosorbide and BPA with a ratio of isosorbide/BPA= 95/5 was observed to have the highest molecular weight among all the isosorbide-based polymers. AL-isosorbide-BPA-PC nanocomposites were synthesized and structurally confirmed by FTIR.

In order to optimize the isosorbide-based PC synthesis, kinetics study was done on the transesterification of BPA and isosorbide. The dependence of reaction temperature and monomer composition on the transesterification rate constant of BPA and isosorbide is studied. The unexpected equilibrium behavior of isosorbide transesterification was revealed. A model was built up for isosorbide and BPA copolymerization, and the reliability of the model was proved.

The understanding of the reaction kinetics is applied to adjust reaction conditions of the copolymerization, a design of random sequenced or large block copolymer of BPA and isosorbide can be achieved.
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Chapter 1

Introduction

Commercial application of bisphenol-A polycarbonate (BPA-PC) is very broad because of its outstanding toughness, transparency, heat resistance, thermal oxidative stability, and electrical properties[1]. For example, BPA-PC is one of the major choices for optical disks such as CDs and DVDs because of its transparency. The combination of high toughness and good transparency makes it a promising material when producing special function glass, such as prescription glasses, aircraft windows, and bullet-resistance glasses. The high refractive index, clarity, and UV absorption make polycarbonate (PC) an ideal material for eyewear including sunglasses, lenses and safety eyewear[2]. The worldwide consumption of PC was about 3.5 million tons in year 2010. With market growth is expected to be more than 8-10% per year. Research to find a more efficient route to improve the current procedures, or find alternatives to produce higher quality PC are ongoing.

In 2007, among the BPA-PC produced, about 90% was made by the phosgene route [3], which was the first commercialized PC production method. The advantage of this route is its moderate reaction condition and easily obtain the raw materials. This process can cause significant environmental impact, including production of large amount of hazardous waste, greenhouse gas emission, and use of toxic reactant. All of these are
significant challenges green chemistry manufacturing, which requires that the use and
generation of hazardous substances be minimized during the design and production
process. Both the raw materials used and the design the reaction and processing must be
considered to fulfill the green chemistry standard. Therefore, it has become an increasing
trend that the phosgene route is being replaced by more sustainable processes to fulfill the
great demand of green chemistry and manufacturing. Alternative polycarbonate
synthesis and processing approaches are the focus of this project. Specifically, solid state
polymerization approaches that may be translated to reactive extrusion processes will be
investigated.

Bisphenol-A (BPA) has a rigid aromatic backbone that provides excellent thermal
stability and mechanical properties and a flexible carbonate linkage that provides
improved processability and toughness to resulting polycarbonate. BPA currently is not a
sustainable monomer from a renewable standard, because it is derived from petroleum;
and from human health aspect, because it is a potential endocrine disrupter[4]. Hydrolytic
degradation of BPA-PC in food packaging material can lead to ingestion of BPA by
humans. The ingestion of BPA by the human body may cause changes in fetuses or
infants and female reproductive issues[5]. In order to fulfill the demands of green
chemistry, bio-derived nontoxic diols which share similar properties with BPA are of
interest for PC production.

A second focus of this research is an investigation of potential renewably sourced
monomers as alternatives to BPA. Monomers were used in this research are shown in
Table 1. Bishydroxymethyl furan (BHMF) and Bisphenol-F (BPF) are furan based
monomers that are derived from biomass. BHMF is commercially available but is thermally unstable at PC synthesis temperature. The BPF was synthesized by Dr. Sucheck’s group in chemistry and biochemistry at University of Toledo. However, polymerization with the BPF was restricted by the source limitation of less than 50mg needed for single polymerization. So polymerization study of with two monomers was limited to preliminary study.

Isosorbide has a rigid ring structure and the hydroxyl end groups needed for PC synthesis. It is derived from glucose, and can be obtained from commercial source. Along with the source renewability aspect, isosorbide is a promising substitute for BPA when considering the human health. It is nontoxic to humans, and has been used as a medication to treat hydrocephalus and glaucoma for years. Isosorbide was chosen for synthesis of both pure polymer and copolymer with BPA in PC and PC nanocomposites production. It was expected that isosorbide based PC (Isosorbide-PC) will fulfill the demand of green chemistry without significant loss of the outstanding thermal and mechanical properties of BPA-PC. The primary focus of this work was to establish synthesis method for isosorbide-PC and isosorbide/BPA copolymers.
Table 1-1 Structures of diols used in this study: Bisphenol-A, isosorbide, BHMF, and BPF

<table>
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<th>Formula</th>
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<td>Bisphenol-A (BPA)</td>
<td>HO-CH(CH$_3$)-CH$_2$OH</td>
</tr>
<tr>
<td>Isosorbide</td>
<td>HO-CH$_2$-O-CH$_2$-OH</td>
</tr>
<tr>
<td>Bishydroxymethyl furan (BHMF)</td>
<td>HO-CH$_2$-O-CH$_2$-OH</td>
</tr>
<tr>
<td>Bisphenol-F (BPF)</td>
<td>HO-CH$_3$-CH$_2$-O-CH$_2$-OH</td>
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Our group has demonstrated that adding aluminum nanowhiskers (Al-NW) to reaction mixture during the solution based PC synthesis can produce transparent BPA-PC nanocomposite with improved mechanical properties compared with the base BPA-PC[6]. In this research, Al-NW were included in the melt phase polymerization of BPA-PC and isosorbide PC to produce composites loadings up to 5wt%. The mechanical, thermal, and optical properties of the composite produced using melt phase polymerization were compared to those solution polymerization composites. Kinetics studies were done on the isosorbide and BPA melt phase polymerization. Although studies has been done on the isosorbide –PC synthesis for decades, the kinetics of the polymerization were seldom reported. The understanding of the rate and equilibrium behavior is very important, it can be applied to optimize the current PC synthesis approaches.
Chapter 2

Research Objective

The overall goal of this research was to synthesis and characterize homo and copolycarbonate with bisphenol-A (BPA) and bio-sourced monomers using melt phase transesterification.

The principle of green engineering and chemistry require that methods be developed that (1) reduce solvent usage and energy usage, (2) incorporate renewable sourced compounds and (3) avoid usage of toxic compounds. In addition, any new material must exhibit similar properties to base material without significant cost increase. The monomers and synthesis methods chosen for this work take into account these principles.

From technical perspective, green engineering requires great reduction of solvent and toxic chemical usage, and at the same time, the important properties such as transparency and toughness can still be maintained. From material perspective, a renewably sourced monomer that has no human health threats, commercially available and of low cost, and structurally similar to BPA would be attractive for further study. This would minimize the cost to obtain the monomer and the cost adjusting the current BPA-PC production system can both be minimized.

The following practical approaches were used to address these challenges to synthesis of
renewably sourced alternatives for BPA-PC produced using interfacial polymerization.

I. Use synthesis and processing strategies that reduce phosgene and solvent usage.

II. Use renewably sourced monomers as alternatives to BPA including starch based isosorbide.

III. Use nanocomposites to moderate thermal and mechanical properties

The following specific objectives using these approaches were pursued in this research.

1. Use melt phase transesterification and solid state polymerization to synthesize homo and copolymers of BPA and renewably sourced monomers.

In this research, PC was synthesized using melt phase transesterification of diols with DPC. Melt phase polycondensation is considered as a more sustainable route than the phosgene route, because it requires very little organic solvent during the polymerization step, the usage of phosgene is avoided, and the only byproduct phenol can be recycled as the material to produce DPC, although more energy is required for the high reaction temperature. The molecular weight of the PC product can be further improved by solid state polymerization, which is also a non-solvent process. Specially, BPA-PC and isosorbide PC were synthesized along with copolymers over range of composition.

2. Investigate the effect of monomer composition and nanofiller loading on reaction kinetics during melt phase transesterification of copolycarbonate.

Isosorbide was chosen in this research as the bio-sourced monomer as an alternate to BPA. Isosorbide is derived from glucose, it has been used in pharmaceutical area for decades, and is available at relatively low cost. Synthesis method of isosorbide polymerization generally mimic the BPA-PC method. An understanding of the isosorbide transesterification polymerization kinetics and equilibrium can provide a better
optimization of the synthesis method. The reaction rate constant, activation energy, and equilibrium constant of BPA and isosorbide based copolymers were studied. A model was developed to predict the concentration change of all components involved in the polymerization. This kinetics data can be used to optimize the co-polymerization of isosorbide and BPA.

3. Investigate the effect of monomer composition and nanofiller loading on thermal and mechanical properties of polycarbonate films.

The impact of inclusion of alumina nanowhiskers (ALNW) within the PC on thermal-mechanical properties was determined up to 2wt% ALNW. In-situ polymerization was used to produce bulk nanocomposites to compare with outcomes of earlier studies using solution based chemistries.
Chapter 3

Literature Review

In this chapter, the methods used to produce BPA-PC and isosorbide-PC will be reviewed. The traditional method to produce BPA-PC is phosgene routes. The non-phosgene routes includes diphenyl carbonate (DPC) route, dimethyl carbonate (DMC) route, carbon monoxide route, ring opening polymerization (ROP), and solid state polymerization (SSP). The methods to produce isosorbide-PC are similar to that of BPA, both solution based and melt phase polymerization methods will be discussed. The promising applications of PC nanocomposites will be introduced. And the previous study about transesterification polymerization of BPA-PC will be discussed.

3.1 Phosgene routes for PC synthesis

The most commonly used commercial method to synthesize BPA-PC is interfacial polycondensation with phosgene (Figure 3-1). BPA react with DPC in the presence of organic solvent and catalyst. The PC product was washed and recovered from the solution and sent to the extruder to get PC pellets. In early years, pyridine was used as both solvent and acid accepter, BPA and phosgene reacted in the presence of a monofunctional phenol to produce PC[1]. The shortcomings of this method were that it is difficult to separate and purify PC from pyridine and its hydrochloride; and the recycle of
pyridine is not commercially favorable.

Bayer in 1958 and G.E. in 1960 improved this process by avoiding the use of pyridine\cite{1}. BPA and phosgene react in the solution of CHCl₂ and NaOH. A mono-functional phenol, such as phenol, is used to control the molecular weight. Triethylamine and other tertiary amines are used as the catalyst because they can act as either bases or nucleophiles to ensure that high molecular weight PC can be synthesized. During the interfacial reaction, phosgene is added to a stirred NaOH, BPA, catalyst and phenol solution. The reaction pH must be carefully controlled as high pH will result in phosgene hydrolysis. Low pH will lead to low reaction rate and low catalyst efficiency\cite{2}. This method is easy to operate because it is solution based, a low reaction temperature (40˚C) is required, and the components used are relatively cheap and easy to purchase. By 1970, all commercial BPA-PC was synthesized using the interfacial technique. The flow diagram and reaction is shown in Figure 3-1.

![Flow diagram and reaction of phosgene route of BPA-PC synthesis](image)

Figure 3-1  Flow diagram and reaction of phosgene route of BPA-PC synthesis
However, there are several drawbacks to interfacial polymerization of BPA-PC. Phosgene and the solvent, CH$_2$Cl$_2$, are both highly toxic. Using large quantity (more than 0.43 t/t of PC) phosgene and CH$_2$Cl$_2$ (more than 10 times the weight of PC produced) in this process is a threat to both environment and human safety. In addition, during synthesis, large amount of salts and acids such as NaCl and HCl are produced. Recovery and treatment of these byproducts must also be addressed and add to process complexity. Residue chloride impurities are difficult to fully avoid in the PC product, which may lead to property defects, such as decreased mechanical strength, of the PC. Alternative approaches that avoid phosgene and chlorinated solvents are of considerable interest. And the new synthesis approaches must produce high purity and Mw PC that is economically competitive with the phosgene route.

### 3.2 Non-Phosgene Route to Produce Polycarbonate

In 1902, Bischoff prepared polycarbonate via transesterification process with hydroquinone and diphenyl carbonate[1]. Fox at GE in 1953 used a similar process to produce BPA-PC. Because of the equipment limitation and absence of proper catalyst at that time, this method was not further investigated or industrially applied. With the development of new processing technique, enhancement in monomer purity, and catalyst improvement, research has been focused on the melt transesterification reaction between BPA and diphenyl carbonate (DPC), or similarly, the reaction of BPA and dimethyl carbonate (DMC) as alternative to the phosgene route. A recent review summarizes routes to synthesize PC without phosgene using CO or CO$_2$ as starting material [7] as
shown in Figure 3-2.

PC can be synthesized by transesterification of BPA with DPC (I), BPA with DMC (II), or BPA directly react with CO (III). DPC and DMC can both be obtained using CO as starting material, which is a renewable resource that is not based on petroleum products. These three routes typically produce low Mw PC or oligomers that are further reacted using solid state polymerization to provide high Mw PC.

3.2.1. **DPC route**

Melt transesterification of BPA with DPC, proceeded easily and efficiently as shown in schemes 3-1 and 3-2, where PhoH stands for phenol[8]. As can be seen from the
schemes, the reaction started when 1 DPC and 1 BPA reacted and formed MpC (1). MpC stands for oligomers with different end groups, one provided by DPC, the other provided by BPA. The other 2 forms of oligomers are DPC(n), which stands for oligomers with both the end group provided DPC; and DH(n), whose end groups are both provided by BPA. In an equal molar ideal reaction, DH(n) and DPC(n) are both intermediate, they’ll convert to MpC(n) by reacting with a different end group. For all the reactions, the only byproduct was phenol.

While the reaction was observed to take place without catalyst, the use of LiOH•H₂O as catalyst with a concentration below 10×10⁻⁴ mol cat/mol BPA resulted in significant increase in conversion of BPA and DPC as the catalyst concentration increased. Ignatov et.al[9] reported that using lanthanum acetylacetonate as an alternative catalyst lead to a lower molecular weight of PC produced, however the thermal stability of product was higher than those produced using LiOH•H₂O catalyst.

\[
\begin{align*}
\text{BPA} + \text{DPC} & \rightarrow \text{MpC}(1) + \text{PhOH} \quad \text{(Scheme3-1)} \\
\text{MpC}(n) + \text{DPC(or BPA)} & \rightarrow \text{DPC}(n)[\text{or DH}(n)] + \text{PhOH} \quad \text{(Scheme3-2-1)} \\
\text{BPA} + \text{DPC}(n) & \rightarrow \text{MpC}(n+1) + \text{PhOH} \quad \text{(Scheme3-2-2)} \\
\text{DH}(n) + \text{DPC} & \rightarrow \text{MpC}(n+1) + \text{PhOH} \quad \text{(Scheme3-2-3)}
\end{align*}
\]
Hsu reported that using 4-(dimethylamino) pyridine (DMAP) as catalyst can produce high quality colorless PC. Side reaction can be greatly avoided if the difference between the heating medium and heating mixture were controlled within a narrow range between 5-15°C [10]. It was determined that the concentration of catalyst, pressure in reactor, and DPC/BPA ratio were all important factors affecting the quality of the PC. Especially, DPC/BPA ratio should be adjusted from system to system. Because the melting point of DPC is 79°C and the boiling point is 306°C at 1 atmosphere, under the reaction condition of more than 180°C and less than 1 torr, the loss of DPC in atmosphere is unavoidable. Without adding excess of DPC, the reaction yield will be reduced, and unbalance end group ratio might constrain the growth of polymer chain [11]. Therefore, a thorough understanding of impact of reactor conditions on reaction kinetics for each monomers used to produce PC is critical. High vacuum is another necessary condition to apply to the reactor to produce PC with high molecular weight. Because the transesterification of BPA with DPC is highly equilibrium restricted. Without the removing of phenol, the reaction
will stop moving forward, so that in most of the research, the reactor pressure was kept below 1 torr.

3.2.2. DMC route

The transesterification reaction of DMC and BPA was shown as a two-step reaction in scheme (3-3) and (3-4)[8]. MmC stands for oligomer with two different end group provided by both BPA and DMC. DMC(1) stands for oligomers with both ends provided by DMC. And DH(n) stands for oligomers with both ends provided by BPA. All of the oligomers can be converted to each other by reacting with different end groups, and methal is the only byproduct of the reactions.

\[
\text{BPA} + \text{DMC} \rightarrow \text{MmC}(1) + \text{CH}_3\text{OH} \quad \text{(Scheme 3-3)}
\]

\[
\text{MmC}(1) + \text{DMC (or BPA)} \rightarrow \text{DmC}(1) [\text{or DH}(1)] + \text{CH}_3\text{OH} \quad \text{(Scheme 3-4)}
\]

Where

\[
\text{MmC}(1) = \text{CH}_3 - \overset{\text{O}}{\text{O}} - \overset{\text{C}}{\text{C}} - \overset{\text{O}}{\text{O}} - \overset{\text{C}}{\text{C}} - \overset{\text{O}}{\text{O}} - \overset{\text{CH}_3}{\text{CH}_3} - \overset{\text{OH}}{\text{O}}
\]

\[
\text{DmC}(1) = \text{CH}_3 - \overset{\text{O}}{\text{O}} - \overset{\text{C}}{\text{C}} - \overset{\text{O}}{\text{O}} - \overset{\text{C}}{\text{C}} - \overset{\text{O}}{\text{O}} - \overset{\text{C}}{\text{C}} - \overset{\text{CH}_3}{\text{CH}_3}
\]

\[
\text{DH}(n) = \overset{\text{O}}{\text{O}} - \overset{\text{C}}{\text{C}} - \overset{\text{O}}{\text{O}} - \overset{\text{C}}{\text{C}} - \overset{\text{O}}{\text{O}} - \overset{\text{C}}{\text{C}} - \overset{\text{O}}{\text{O}} - \overset{\text{H}}{\text{H}}
\]

This reaction was of low efficiency, because of the equilibrium restriction of. In order to overcome the equilibrium constraint, more complex reaction conditions are required than
for the DPC system. For example, Haba et al. [12] reported that the process should be run with a large excess of DMC (68 times mole of BPA) for as long as 48 hours to overcome the equilibrium limitation. Lewis acid such as titanium alkoxides are the commonly used catalysts. And after comparing the stability and facile recovery and regeneration, silica-supported titania was found to be the best catalyst for transesterification of BPA and DMC. There was a significant yield of methylated bisphenol-A as a byproduct. Recover and reuse of DMC would be involved, which can facilitate the equilibrium shifting to the desired direction.

Titanium catalyst, BuSn₂O, and bis(4-chlororocabonylphenyl) dimethylsilane were all acceptable catalyst used in reaction of DMC and BPA. Especially, using bis(4-chlororocabonylphenyl) dimethylsilane as catalyst leads to 94% yield of PC and the reaction temperature is 0°C, the reaction time is 1 hour. Because of equilibrium limitations and need to use excess DMC, this route is currently not practical for scale up commercially.

3.2.3. **CO route**

The direct oxidative carbonylation of BPA with CO/O₂ is considered to be the optimal green route to produce BPA-PC, as this is a direct process avoiding the use of DMC and DPC as intermediates. The reaction is shown in Scheme 3-5. However, research concentrating on this route is very limited. The main reason is that the hydroxyl-terminated oligomers produced are the least reactive in the polycondensation step. Different catalytic systems, such as Pd-Cu redox catalytic system and Pd-Ce system, have been tried. But the conversion rate of BPA was still low, and the percentage of byproducts can't be reduced to a desired level.
BPA + CO → DH(n) + H₂O  

(Scheme 3-5)

\[
\text{DH}(n) = \left[ \begin{array}{c}
\text{O} \\
\text{C}_\text{C3H7}
\end{array} \right] \left[ \begin{array}{c}
\text{O} \\
\text{C}_\text{Cl3}
\end{array} \right] \cdot \text{O} \cdot \text{O} \cdot \text{O}
\]

3.2.4. Comparison of non-phosgene transesterification methods

A comparison of different non-phosgene methods to produce BPA-PC was listed in Table 3-1. From the table, it can be concluded that, the transesterification of BPA and DPC is the most effective one. Less reaction time, and less excess of carbonyl source were required to produce high molecular weight PC with better yield and conversion rate. The DMC route was restricted by serious equilibrium limitation, so that large excess of DMC was required to recycle for a long reaction time. The CO route was limited by its critical reaction condition, but the conversion and yield was still better than that of DMC route.

In summary, each of the three routes to produce PC has advantages and disadvantages. In the long term, the direct oxidative carbonylation of BPA with CO/O₂ is considered to be the most promising method as it greatly reduces complexity the process from CO to PC.

The DPC route is the best developed method, if efficiency is being considered; this should the first choice. The reaction time is short, which leads to the saving of energy usage. No phosgene is involvend, and the usage of organic solvent is minimized. It will allow the easiest translation to renewably sourced monomers and nanocomposites and will be focus of this research.

Ignatov’s approach was chosen in this research, because high molecular weight PC was synthesized using this method. And the equipment setup used in that research are all available in our lab.
Table 3-1 Examples of experimental methods and conversions of BPA-PC synthesized using DPC, DMC, and CO

<table>
<thead>
<tr>
<th>Carbonyl Source</th>
<th>Excess of Carbonyl Source</th>
<th>Catalyst</th>
<th>Reaction Conditions</th>
<th>Reaction Time</th>
<th>Conversion yield</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>DPC</td>
<td>10%</td>
<td>La(acac)₃</td>
<td>165-260 °C, 20-25 mmHg vacuum</td>
<td>2</td>
<td>Mw= 31500</td>
<td>Ignatov et al.[13, 14]</td>
</tr>
<tr>
<td>DPC</td>
<td>5%</td>
<td>LiOH</td>
<td>230°C, 5mmHg vacuum</td>
<td>2.5</td>
<td>Mw= 1600</td>
<td>Woo et al.[15]</td>
</tr>
<tr>
<td>DMC</td>
<td>580%</td>
<td>(Bu₂SnCl)₂O₂</td>
<td>215-260°C</td>
<td>48</td>
<td>74% BPA conversion, 22% PC oligomer yield</td>
<td>Haba et al.[12]</td>
</tr>
<tr>
<td>DMC</td>
<td>N/A</td>
<td>TiO₂/SiO₂</td>
<td>200°C</td>
<td>7</td>
<td>10%-20% BPA conversion, 10-20% PC oligomer yield</td>
<td>Kim and Lee[8]</td>
</tr>
<tr>
<td>CO</td>
<td>N/A</td>
<td>PdCl₂/Cu(OAc)₂/TBAB/HQ</td>
<td>100°C, 60kg/cm² CO, 3kg/cm² CO</td>
<td>24</td>
<td>50% PC yield</td>
<td>Goyal et al.</td>
</tr>
<tr>
<td>CO</td>
<td>N/A</td>
<td>Mn(TMHD)₃/HQ/(Ph₃P = )₂NBr</td>
<td>100°C, 60kg/cm², 6MPa CO, 0.3MPa O₂</td>
<td>24</td>
<td>86% oligomer yield; Mn= 3300</td>
<td>Isii et al.</td>
</tr>
</tbody>
</table>

3.2.5. Ring opening polymerization

Ring opening polymerization (ROP) is a can be used to produce PC and can be transferred to reactive extrusion processing. Cyclic PC oligomers are prepared from BPA. Single chain PC with high molecular weight can be obtained by heating the oligomer at
200°C with the presence of catalyst[16]. The advantage of this method is that it is a phosgene and solvent free polymerization process, and there’s no side reaction during the polymerization. High purity and high molecular weight PC can be synthesized by relatively simple method compared to other synthesis processes mentioned above [17, 18]. The study of the preparation of cyclic oligomers from the biosourced monomers would be complicated and beyond scope of this project.

3.2.6. Solid state polymerization

Solid state polymerization (SSP) is a polycondensation process that often follows melt phase polymerization, and has been widely used in PET, nylon and PBT production[19]. Enhancement of molecular weight can be obtained follow heating the polymer at a temperature between glass transition temperature and melting temperature[19]. The SSP reaction of PC produced using melt phase transesterification with DPC is shown in Figure 3-3.

![Figure 3-3 SSP reaction of PC produced using DPC](image)

For this process, prepolymer was synthesized used DPC and BPA using LiOH•H2O as catalyst. Solvent-induces crystallization was applied. The crystallized prepolymer particles were placed in high temperature vessel. With N2 as sweep fluid to remove phenol from the reactor, PC with a molecular weight of 35000g/mol and above has been produced.
Two kinds of end group, phenyl carbonate group, which is provided by the DPC in melt phase polymerization, and hydroxyl group, which originated from the BPA, react with each other to increase molecular weight. Phenol is generated as by product. SSP is typically performed under vacuum or nitrogen sweep to enhance the rate of phenol removal, and shift to equilibrium to high concentration.

Researches have shown that there are several factors that may affect the molecular weight of SSP product. Among all the factors, particle size, fluid gas, and surface porosity are related to mass and heat transfer limitation; reaction temperature, and relative ratio of end groups were reaction kinetics related. In this research, PC and nanocomposites used in SSP are all in fine powder form, the transfer problems will not be a crucial limitation. However, for eventual scale up to commercially processing, the solid stating would be performed using pellets and mass transfer limitation will be more important.

In order to understand the reaction kinetics, a diffusion-reaction model for SSP of polycarbonate was established by Ye and Kim. They demonstrated that the end group ratio of prepolymer had a dominant effect on the Mw after SSP[20]. In order to achieve high Mw BPA-PC after SSP, it is crucial to keep the ratio of phenyl carbonate end group and hydroxyl end group of the oligomers close to 1:1[21]. Thus, it is important to adjust the ratio of diol (i.e. BPA) and DPC during melt phase polymerization, because the ratio of DPC loss during melt phase polymerization is different from system to system.

Once the reaction kinetics are well understood, melt phase/solid state polymerization can be scaled up using reactive extrusion (REX). REX has been applied in the commercial polymerization, nanocomposites synthesis, and polymer blends process using several polymers, including PC and PET [22]. It is a promising sustainable process because of its
ability to synthesize and extrude ready-to-use polymers and composites. Solvent use is avoided and energy is saved, so REX is considered a cost effective route. Using REX can also reduce the heat and mass transfer problems encountered during melt phase reactions, high molecular weight and high quality polymer product can be produced efficiently. REX studies are beyond scope of this work but goal will be to target processes that can be translated to this method.

3.2.7. Industrial non-phosgene PC production

In a recent review article, Fukuoka et al. summarized the Asahi Kesei process, the world's first successfully industrialized non-phosgene process using CO₂ as starting material as shown in Figure 3-4 [3]. And a general diagram of Asahi Kesei is shown in Figure 3-5.

![Figure 3-4 General diagram of Asahi Kesei's non-phosgene PC synthesis process](image)

The reactivity of CO₂ is very low, compare to CO. CO₂ is chemically splitted into CO and O in this process. And the separated CO is further applied to the PC synthesis; O is used to the monoethylene glycol (MEG) production.
In Figure 3-5, reaction 1 represents CO$_2$ reacts with ethylene oxide (EO) to produce ethylene carbonate (EC). In reaction 2, EC is used with methanol to produce DMC and monoethylene glycol (MEG). MEG can be kept as a valuable byproduct, and DMC is further utilized to react with phenol to produce DPC and methanol. In the last reaction, PC is obtained through the reaction of DPC and bisphenol-A.

This method is fully sustainable and environmentally favorable for these reasons:

1) The use of phosgene and chloride compounds are both avoided. And waste water treatment is minimized.

2) CO$_2$ can be used as the starting material, which not only solves greenhouse gas pollution problem, but also reduces the material cost.

3) All intermediates can either be completely consumed or recycled as raw reactants in the next or previous reaction. The only raw materials involved are CO$_2$, EO and BPA. EO is the raw material for ethylene glycol, which is used in industry to
produce PET bottles. BPA is the traditional raw material to synthesis BPA-PC. The raw materials are all readily available.

4) High yields and high selectivity are achieved in all the steps of this process. It is mentioned that the PC products obtained through Asahi Kasei Process possess several good qualities such as free chloride containing, mold deposits and good moldability. At this point, over 210,000 tons of PC produced each year worldwide has been made through this method. This demonstrates that a sustainable polymerization pathway to BPA-PC is available that takes advantage of CO₂ as feedstock for polymer.

3.3 Isosorbide PC

Isosorbide, the structure of which is shown in Table 1-1, is derived from glucose by dehydration of D-isosorbide. It has been produced in large quantity for use in medicine, and is considered to be a promising byproduct of the starch industry[23]. Isosorbide is a chemically stable diol due to its rigid structure. A lot of studies has been done on synthesizing bio-polymer using isosorbide as the monomer, including polyester [24-26], polyamide[27-29], poly(ester amide)s[30, 31], polyurethane[32-35], polyethers[25, 36], and polycarbonate.

Isosorbide-PC has been produced through solution based polycondensation using method developed to BPA-PC. Unlike BPA, isosorbide is highly hydrophilic, which makes it difficult to diffuse into organic phase, where the solution based transesterification polymerization occurs. So that the traditional BPA-PC polymerization method cannot be directly transferred to the synthesis of isosorbide-PC through interfacial polymerization.
3.3.1. Solution based isosorbide-PC synthesis

Terao et al. used the traditional phosgene method developed or BPA-PC to produce isosorbide-PC. In this work, isosorbide was dissolved in acetonitrile and pyridine react with equal molar of phosgene at 50°C for 2h[37]. The molecular weight of product recovered from the solution was 19,000. Then the same experiment was carried out using 20% mol excess of phosgene charged into the reactor for 9h. This time the Mn of product was improved to 81,000. In this method, it was proved that the diffusion problem of isosorbide can be solved by significantly increasing the solution based polycondensation reaction time.

Chatti et al. studied the following methods to synthesize isosorbide-PC [38]. Unfortunately, the first method, the melt phase transesterification with DPC method failed, no BPA-PC was synthesized.

Two solution based polymerization approaches are shown in Figure 3-6, where isosorbide react with diphosgene in organic solution at low temperature. In the second method, triethylamine was added to the solution of isosorbide and pyridine, and reacted with the solution of diphosgene and dichlorofomethane. During the solution mixing stage, the temperature should be controlled at no higher than 10°C. The reaction lasted 24h at 20°C. It was found out that because diphosgene can be decomposed by pyridine, an excess of diphosgene was required to synthesis high Mn isosorbide-PC. In this work, 20% excess of diphosgene was shown to be the ideal amount to control the molecular weight.
In the second approach, isosorbide was first dissolved in dioxane, then a solution of pyridine was added, the rest of the procedure was similar to the method described above. Barely any cyclic carbonate was observed after analyzing using NMR. The author suggested that because of the rigid and low mobility structure, at low temperature, the formation of cyclic product was prevented, while at the same time the chain growth was not prohibited.

3.3.2. Melt phase isosorbide-PC synthesis

The melt phase transesterification method has been studied by several groups. As mentioned above, Chatti tried melt phase polycondensation using dimethyl carbonates and diethyl carbonate reacted for 200°C, KPtBu was added as the catalyst. No ISO-PC was recovered from the reactor after 2h of reaction.

Ola Beiku et al. carried out the reaction using isosorbide reacted with DPC at 200°C[40], using NaOMe as the catalyst, under reduced pressure for 2h. After precipitation, about 95% yield of polymer was recovered from the solution.

Li et al. proved that isosorbide-PC was synthesized using DMC through a 2-step polycondensation shown in Figure 3-7[41]. The first stage is transesterification stage, DMC and isosorbide was heated at 98°C for 6h. The temperature was gradually increased.
to 180°C and maintained for 1h. In the second polycondensation stage, the temperature of the reactor was increased to 240°C and maintained for 5h.

Figure 3- 7 Reaction scheme of the 2-step isosorbide-PC synthesis method using DMC [41]

The effect of different catalyst was compared, and the polymer synthesized using LiAcac was shown to have the highest Mn and Mw. Mn of isosorbide-PC synthesized at different polycondensation temperatures were measured, and the result showed that as polycondensation temperatures increased, the Mn increased until it reached 240°C, after that temperature, the Mn decreased as the reaction temperature increased. The other
parameter studied is the DMC feed ratio. Because the reaction took place at a temperature much higher than the boiling point of DMC for long time, the loss of DMC is unavoidable. In their study, the highest DMC ratio, which was 10 times the isosorbide feed, turned out to give the highest molecular weight. A trend of increasing molecular weight as DMC ratio increased was observed, it would be more convincible if DMC ratios more than 1:10 were also reported to get to the conclusion that 1:10 was the ideal feed ratio.

In summary, synthesis method and properties of the isosorbide-PC product of the methods mentioned above are reported in Table 3-2. Comparing the results, it was observed that, for isosorbide-PCs with high molecular weight, high glass transition temperatures were always obtained; compare to the Tg of BPA-PC was about 150°C. This can be explained by the stiff and rigid ring structure of isosorbide monomer leaded to low mobility of the isosorbide-PC polymer chain.

The highest Mn isosorbide-PC was synthesized using solution based polycondensation, but the reaction time was very long. The studies of melt phase isosorbide-PC were as extensive as the solution based synthesis, the proper reaction time, temperature and procedure were all under study.
### Table 3: Comparison of different isosorbide-PC synthesis methods

<table>
<thead>
<tr>
<th>Synthesis Method</th>
<th>Reaction Temperature(°C)</th>
<th>Reaction Time (h)</th>
<th>Tg(°C)</th>
<th>Mn</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Solvent based polymerization</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ISO:phosgene=1:1 with pyridine</td>
<td>50</td>
<td>2</td>
<td>163</td>
<td>19,000</td>
<td>[37]</td>
</tr>
<tr>
<td>ISO:phosgene=1:1.2 with pyridine</td>
<td>50</td>
<td>9</td>
<td>175</td>
<td>81,000</td>
<td>[37]</td>
</tr>
<tr>
<td>ISO:diphosgene=2:1 with pyridine</td>
<td>20</td>
<td>24</td>
<td>117</td>
<td>4,500</td>
<td>[38]</td>
</tr>
<tr>
<td>ISO:diphosgene=2:1.2 with pyridine</td>
<td>20</td>
<td>24</td>
<td>163</td>
<td>50,000</td>
<td>[38]</td>
</tr>
<tr>
<td><strong>Melt phase polymerization</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ISO:diphosgene=2:1.05 with dioxane and pyridine</td>
<td>20</td>
<td>24</td>
<td>146</td>
<td>30,000</td>
<td>[38]</td>
</tr>
<tr>
<td>ISO:DPC=1:1</td>
<td>200</td>
<td>2</td>
<td>158</td>
<td>9500</td>
<td>[42]</td>
</tr>
<tr>
<td>ISO:DMC=1:7.5</td>
<td>240</td>
<td>5</td>
<td>166</td>
<td>28700</td>
<td>[41]</td>
</tr>
</tbody>
</table>

#### 3.3.3. Isosorbide-based copolycarbonates

Isosorbide is a promising alternative to BPA. It has a rigid ring structure, which ensures the high strength and high glass transition temperature of isosorbide-PC. But unlike BPA, there is no flexible carbonyl group in isosorbide structure, which might lead to the lack of mobility of the PC produced and impact toughness. In order to synthesize alternative PC with high strength and Tg, and maintain the flexibility and toughness of BPA-PC, copolymers of isosorbide with BPA, or other aliphatic diol was of are of particular interest.
After progress were made in the isosorbide-PC synthesis, Chatti et al. applied the same procedure to the copolymerization study using various diols including bisphenol-A, 3,3’-dimethyl bisphenol-A, bisphenol-C, 1,3-bis(4hydroxybenzoyloxy)propane, and 1,4-cyclohexane diol using equal molar of isosorbide: diol [43]. The copolymer was shown to be random sequenced copolymer by $^{13}$C NMR spectroscopy. And it was found out that the limitation of copolymer chain growth was cyclization. Another groups of copolymers were produced using isosorbide react with bisphenol A bischloroformiate, and BPA with isosorbide bischloroformiate. This time alternating sequence was observed instead of random sequence. The Tg of the alternating copolymers were 15°C or 25°C higher than those of the random ones. But large amount of cyclic PCs were also found after analyzing the procedure using MALDI.

Terao et al. also extended their interfacial polycondensation work of pure isosorbide-PC synthesis to copolymer study[37], where aliphatic poly(ester-carbonate) were synthesized, transparent films of the polymer were made, and tensile yield strength was measured as 65MPa.

In Betiku’s work, block copolymer of isosorbide-PC and polylactide (PLA) was made by synthesizing the two polymers separately[40], mixing them in either solvent and melt mixing, followed by transesterification of PLA isosorbide-PC at 240°C. The advantage of isosorbide-PC was its high Tg, the idea of this study was to synthesize a copolymer to improve the Tg of PLA. But because of the insufficient study of melt phase isosorbide-PC synthesis, the low Mn of isosorbide-PC leaded to a significant decrease of the copolymer Mn.

The two step polymerization using DMC was also used to synthesize isosorbide-based
copolymers using the same method as pure isosorbide-PC synthesis [41]. The reaction was shown in Figure 3-8. In the first stage, isosorbide and aliphatic diol were reacted with DMC separately to form oligomer. In the second stage, high heat and high vacuum were applied to the two oligomers for 11 h. The NMR spectra confirmed the random microstructure of the copolymers. Because of the adding of aliphatic diol, the Tg of copolymer was significantly decreased, the further dynamic mechanical analysis proved that compared to the pure isosorbide-PC, the incorporation of linear structure changed dynamic mechanical properties dramatically. The rigidity decreased as the linear diol composition increased in the copolymer.
In recent patents prepared by Sabic Co. BPA, isosorbide, various diacid or diol, and bis (methylsalicyl) carbonate were added into the reactor, temperature was gradually increased to 270°C at reduced pressure[44, 45]. Both small scale batch reactor and large scale continues process reactive extruder were used. In this study, copolymers with compositions within the range of: 55% to 97.5% of isosorbide, 2.5% to 15% of aliphatic unit, 0 to 42.5% of additional BPA were synthesized and compared. It was found out that when longer chain aliphatic diacid monomer was added to the
copolymer composition, higher molecular weight polymers were more likely to be produced. This may be due to the high mobility of longer chain aliphatic diacid at high temperature.

With higher concentration of isosorbide in the copolymer composition, a higher Tg was observed, for samples with isosorbide less than 70%, the Tg of the copolymers fell below 100°C.

For copolymers with the same aliphatic chain length, a higher molecular weight and lower Tg were observed with additive of increasing amount aliphatic monomer. This observation was consistent with Li et al’s work [41]. So that it is very important to modify the stiffness of isosorbide with proper amount of BPA and aliphatic diol without losing the high Tg.

Among all the samples, it was observed that copolymer with 80% isosorbide, 13% BPA, and 7% aliphatic diacid monomer showed the ideal combination of high Tg and high molecular weight.

Lee et al. studied the effect of the thermal stability, rigidity, and strength were affected by the feeding ratio of isosorbide and BPA in the copolymer containing only the two monomers[42]. Copolymer with an isosorbide: BPA ratio from 20 to 2 were synthesized using transesterification polymerization with DPC. During the reaction, the reaction temperature was gradually increased from 187°C to 270°C for 2 hours, with high vacuum was applied to distill by product phenol. The copolymer product were casted into films using heat pressing, and analyzed using IR to confirm the structure. For all the copolymers, high Tg values (153-173°C) were observed, the storage modulus were between 2.6 to 3.2 GPa at 25°C, and increased as isosorbide concentration increased. It
was also observed that, the higher concentration of isosorbide in the monomer content, the higher Mn was measured. In this study, the copolymer with a isosorbide:BPA ratio of 20 exhibited the highest Tg and Mn at the same time. Lee extended this method to explore polymer nanocomposite with nanoclay added during the processing stage.

Table 3- 3 Comparison of different isosorbide copolymer synthesis methods and properties

<table>
<thead>
<tr>
<th>Monomer</th>
<th>Carbonyl source</th>
<th>Reaction Temperature (°C)</th>
<th>Reaction Time (h)</th>
<th>Tg (°C)</th>
<th>Mn</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>ISO: BPA=1:1</td>
<td>Diphosgene</td>
<td>20</td>
<td>48</td>
<td>135</td>
<td>N/A</td>
<td>[38]</td>
</tr>
<tr>
<td>ISO: bisphenol C=1:1</td>
<td>Diphosgene</td>
<td>20</td>
<td>48</td>
<td>175</td>
<td>N/A</td>
<td>[43]</td>
</tr>
<tr>
<td>ISO: 1,4-butanediol=1:0.86</td>
<td>DMC</td>
<td>200</td>
<td>11</td>
<td>70</td>
<td>34400</td>
<td></td>
</tr>
<tr>
<td>ISO: 1.5-petanediol=1:1.09</td>
<td>DMC</td>
<td>200</td>
<td>11</td>
<td>48</td>
<td>27100</td>
<td></td>
</tr>
<tr>
<td>ISO: 1.6-hexanediol=1:0.95</td>
<td>DMC</td>
<td>200</td>
<td>11</td>
<td>46</td>
<td>29800</td>
<td></td>
</tr>
<tr>
<td>ISO:: 1,4-cyclohexane dimethanol=1:1.14</td>
<td>DMC</td>
<td>200</td>
<td>11</td>
<td>88</td>
<td>18700</td>
<td>[41]</td>
</tr>
<tr>
<td>ISO:BPA=20:1</td>
<td>DPC</td>
<td>187-270</td>
<td>3</td>
<td>173</td>
<td>33000</td>
<td></td>
</tr>
<tr>
<td>ISO:BPA=2:1</td>
<td>DPC</td>
<td>187-270</td>
<td>3</td>
<td>154</td>
<td>13000</td>
<td></td>
</tr>
<tr>
<td>ISO:BPA=10:1</td>
<td>DPC</td>
<td>187-270</td>
<td>3</td>
<td>170</td>
<td>32000</td>
<td></td>
</tr>
<tr>
<td>ISO:BPA:C12 diacid=71:12:17</td>
<td>bis (methylsalicyl carbonate)</td>
<td>180-270</td>
<td>0.6</td>
<td>97</td>
<td>16700</td>
<td></td>
</tr>
<tr>
<td>ISO:C36 diacid=93:7</td>
<td>bis (methylsalicyl carbonate)</td>
<td>180-270</td>
<td>0.6</td>
<td>120</td>
<td>26100</td>
<td></td>
</tr>
<tr>
<td>ISO:BPA:C36 diacid=80:13:7</td>
<td>bis (methylsalicyl carbonate)</td>
<td>180-270</td>
<td>0.6</td>
<td>120</td>
<td>25929</td>
<td></td>
</tr>
<tr>
<td>ISO:BPA:C36 diacid=55:30:15</td>
<td>bis (methylsalicyl carbonate)</td>
<td>180-270</td>
<td>0.6</td>
<td>83</td>
<td>8600</td>
<td>[44]</td>
</tr>
</tbody>
</table>


In summary, the methods used to synthesize isosorbide-based copolymer and outcomes were exhibited in Table 3-3. From the table it can be concluded that when synthesizing the isosorbide-based copolymer, solution based polycondensation was limited by the fact that isosorbide and BPA behaved quite differently when diffusing into organic solvent. The copolymers produced were of low molecular weight, even with longer of reaction time.

Several studies have focused on melt phase transesterification BPA, aliphatic diol or diacid were used to modify the stiffness of isosorbide-PC. The major challenge here was how to control different monomer contents to increase the mobility of copolymers without significantly dropping of glass transition temperature.

The three carbonate sources required different reaction time. DMC was the least reactive one, so the polymerization with DMC took the longest time. The reason for Jansen et al. greatly shortened the reaction time maybe contributed to a different carbonate source, and their effective batch reactor followed by a reactive extruder. Lee et al. used DPC as carbonate source, with small scale reaction that took longer than the Jansen’s, but the molecular weight of the copolymers were way higher than all of the other systems. In both studies, the higher isosorbide content used, the higher molecular weight for copolymer.

Comparing the diphosgene and DMC reactions, it was clear that with equal mole aliphatic diol adding and isosorbide, there was a sharp drop in glass transition temperature was unavoidable, meanwhile the molecular weight can be maintained at a relative high value with increasing reaction time. It was possible that the molecular weight of the bis (methylsaliicyl) carbonate group copolymers can be further increased by
increasing the reaction temperature.

3.4 PC nanocomposite

Ceramic polymer nanocomposite has been an interesting research area because of the potential for improvement in the mechanical properties compared to the base polymer. The enhancement of the mechanical strength often comes with loss of other properties (ie. transparency). The main factor that causes the loss of transparency is light scattering because of local refractive index variations [46, 47]. To minimize the light scattering, nanoscale fillers that are well dispersed in the polymer matrix must be used [48, 49]. Several nanofillers have been studied to improve the properties of polymers, including nanoclay, carbon nanofibers, carbon nanotubes, and polyhedral oligomeric silsequioxane (POSS) [50, 51]. In most of the studies, properties of interests were enhanced with the increase of nanofillers weight percentage up to a point. But the high surface to volume ratio of nanofillers typically results in formation of agglomerates. Thus, an increase in the nanofillers loading often leads to poor dispersion of nanofillers in the polymer matrix and degradation of properties.

Alumina nanowhiskers are of interest in this research because of their small size, high strength, high wear resistance, and presence of the reactive hydroxyl groups on the surface that allow grafting of functional groups. It has been shown by our group that Al-NW can be successfully incorporated within BPA-PC using solution based in-situ polymerization process. PC chain was covalently bonded to the surface of alumina nanowhiskers which aided in dispersion and interactions at the interface between PC and AL-NW. Films made from the nanocomposite showed significant enhancement in mechanical properties,
without significant loss of transparency as shown in Figure 3-9 and 3-10 [6]. However, this work was limited to solution based chemistry.

Figure 3- 9 Tensile strength of AL-PC as a function of AL-NW loading with AL-PC in-situ polymerized at (a)55°C, (b) 40°C, (c) 20°C, and (d) blended at processing stage, without in-situ polymerization[6]

In this study, a master batch of 5wt% ALNW in BPA-PC was synthesized and dimuted with commercial BPA-PC. The effect of synthesis temperature was reported.

For nanocomposite synthesized at given reaction temperature, the tensile stress at yield and young’s modulus both increased significantly. The adhesion and dispersion of stiff AL-NW in the polymer matrix was proved to greatly improve by in-situ polymerization.

Sample produced at higher reaction temperature exhibited higher yield tensile stress and Young’s modulus at a given loading. This can be explained by the fact that as the reaction temperature increased, the reactivity of AL-NW hydroxyl groups increased, which should lead to long polymer chain. This will enhance both dispersion and wetting
between matrix and nanowhiskers surface.

In Hakimelahi’s research, it was observed that, for AL-PC synthesized from in-situ polymerization, with AL-NW loadings of 0.5%-2%, the transparency of films made from the nanocomposites were still maintained. However, if the AL-NW and high molecular weight PC were blended simply during processing stage, which means without in-situ polymerization, a significant haziness was observed from the film made following same the procedure. This light diffraction behavior confirmed the presence of large agglomerates within the composite, without the in-situ polymerization.

According to the study discussed above, transparent and reinforced films can be made with BPA-PC by solution based polymerization. In my research, the goal was to apply the melt phase transesterification to in-situ polymerization of bio-sourced nanocomposites. The effect of nanocomposite on reaction kinetics were studied.
3.5 Transesterification polymerization kinetics

The kinetics study of melt phase transesterification polymerization of BPA with DPC has been studied for decades since the early 1970s. In Kim and Choi’s work[52], BPA and DPC were added to a batch reactor and heated to 250°C. Small amount of reaction mixture was taken out from the reactor during the reaction at regular times integral. The composition of the mixture was analyzed by HPLC. And it was mentioned that, there is 7% reproducibility when using HPLC to calculate the composition. A comparison of polymerization with or without catalyst was made on BPA and DPC. It was found out that the reaction can proceed to some extent with the absence of catalyst. The reaction rate and activation energy were greatly improved by addition of LiOH·H₂O as the catalyst. Effective models of both the transesterification reaction and the vapor-liquid equilibrium in the reactor were successfully proposed and confirmed.

This model has been widely accepted, and used as the basis of most of the later developed BPA-PC transesterification models [13, 53]

After calculating the rate constant at 210°C, 230°C, and 250°C. The forward and backward reaction rate constant calculated in this research were shown as followed:

For the uncatalyzed reaction,

\[
\begin{align*}
\text{k} &= (3.11 \pm 0.01) \times 10^7 \exp \left(\frac{-25300 \pm 100}{RT}\right) \text{L}^2/(\text{mol min}) \\
\text{k}' &= (2.03 \pm 0.01) \times 10^{15} \exp \left(\frac{-45000 \pm 300}{RT}\right) \text{L}^2/(\text{mol min})
\end{align*}
\]

The equilibrium constants at 210°C, 230°C, and 250°C are 12.51, 5.53, and 2.6 separately. and for the reaction catalyzed by LiOH·H₂O,

\[
\text{k} = (8.50 \pm 0.01) \times 10^7 \exp \left(\frac{-14200 \pm 400}{RT}\right) \text{L}^2/(\text{mol min})
\]

37
\[ k' = (7.31 \pm 0.01) \times 10^6 \exp \left[\frac{-12100 \pm 300}{RT}\right] \text{L}^2/(\text{mol min}) \]

The equilibrium constants at 180°C, 210°C, and 230°C are 1.30, and 1.42 separately.

Comparing those two sets of values, the activation energies of the catalyzed reaction was way smaller than the uncatalyzed one. And the equilibrium constants of the uncatalyzed reaction changed significantly as temperature changed, but for the catalyzed one, the change was much smaller.

With the understanding of the BPA and DPC transesterification kinetics, Kim and Choi continued the kinetics studied in a semi-batch reactor[54], where gradually increased reaction temperature and reduced pressure were applied. The model was adjusted to modify the conditions close to the real synthesis procedures. The reliability of the model was also proved by the agreement between the experimental data and simulated results. Specially, the effect of DPC loss during the reaction was studied. It was found out a small amount DPC vaporization did not have significant effect on the BPA-PC molecular weight was not significant, but the ratio of the carbonyl end group and hydroxyl end group was greatly depended on the amount of DPC excess.

The polymerization process of BPA-PC was shown to be equilibrium restricted. The degree of oligomerization was quite limited in the batch reactor because the large amount of phenol residue. It was believed in the real synthesis batch, gradually increased temperature and continuously high vacuum was able to facilitate the reaction moving to the forward reaction, and PC product with high molecular weight can be obtained [15].

While Ignatov et al.[14] developed a simpler model for the kinetics measurement. It was assumed the reaction was a second order reaction with respect of DPC and BPA in the absence of catalyst concentration change. With equal molar of BPA and DPC added
initially, it was assumed the concentration of hydroxyl end group and phenolic end group were always equal at any time during the reaction. The reactivity of end groups was not affected by the chain length. In this research, the kinetics model we used was borrowed from this research. Ignatov et al. compared the catalytic activity of different kinds of catalyst at 165°C, which was considered as the starting temperature of BPA and DPC transesterification polymerization. It was found out that alkaline-earth and alkaline metals were the most active catalysts, and organic heterocyclic compounds were the least active ones.

Other than BPA and DPC, transesterification polymerization of other monomer has also been investigated. Godinez and Lozano[55] studied the kinetics parameters of bisphenol acetophenone and DPC transesterification. Kim and Choi’s model was borrowed. HPLC-MS was chosen to measure the concentrations. The repeatability of the data was 20%, which was not quite ideal. The concentration profiles of all the compounds in the reactant mixtures as a function of time were reported and compared with values predicted by the model. For most of the compounds, the experimental data agreed with the predicted data. But for some of the oligomer, equilibrium was not reached as predicted. The values of rate constant and activation energy of bisphenol acetophenone and DPC transesterification were in the similar range of that of BPA and DPC. This makes in a potential comonomer in the production of high-optical-quality resins.
Chapter 4

Experimental

This chapter presents a detailed description of the general experimental procedure and the characterization techniques used for this project.

4.1 Materials

Aluminum oxide nanowhiskers with a diameter of 2-4nm, length of 2800 nm and surface area of 350-720 m²/g were purchased from Sigma-Aldrich. The isosorbide (98%) was purchased from Sigma-Aldrich, and purified using recrystallization from methanol. Bisphenol-A(99%), diphenol carbonate, the catalyst 4-(dimethylamino) pyridine (DMAP), n-Butyltinoxidehydroxid and BPA-PC with molecular weight of 64,000 were purchased from Sigma-Aldrich and used without further purification.

4.2 Purification of isosorbide

Isosorbide was purified by crystallization from methanol[56]. Specifically, 14g isosorbide was dissolved in 6 ml methanol, and the solution was kept at -14°C for 12 hours. Pure white crystal isosorbide were recovered and washed with cold methanol. The recrystallized isosorbide was dried in a vacuum oven overnight at room temperature.
4.3 BPA-PC nanocomposite synthesis through melt phase polymerization

The method Ignatov et al.[13, 14] for melt phase polymerization was selected in this research. This method was chosen because it allows effective production of BPA-PC through the transesterification of BPA with DPC, and the access of the experimental setups involved were all confirmed.

In this method a 3-necked flask was placed in a heating mantel controlled by a digital regulator. The 3 necks were connected to a mechanical stir, a nitrogen inlet and a distillation system separately as shown in Figure 4-1.

Before the in-situ polymerization, the reactor was tested by running transesterifications of BPA with DPC. For this reaction, 5g of BPA and different molar ratio of DPC were used. Because the excess of DPC is a critical parameter to in the synthesis, the loss of DPC is different from system to system. Uneven molar of BPA and DPC will cause the unbalanced end group, and lead to restriction of polymer chain growth.

Polymerizations with a DPC: BPA ratio of 1, 1.05, 1.1, 1.15, and 1.2 were tested. A 1.15 molar ratio gave a yield of 7.1g PC produced was proved to be the most efficient one. The pure BPA-PC and in-situ polymerization used this feed ratio.

For the in-situ transesterification, 0.35 g of ALNW (calculated as 5% by weight based on the 7g yield) was blended with 5 g of BPA, and added to the reactor. The reactor was heated to 160°C under continuous nitrogen flow. DPC at a molar ratio of 1.15 to BPA and 50ppm of the catalyst, 4-(dimethylamino) pyridine (DMAP), was added to the reactor. The mixture was stirred under vacuum, and the temperature was gradually increased to 260°C for 1.5 hours. The reaction was maintained at 260°C for 2 hours. The heat was turned off and
reactor was cooled to room temperature under vacuum. Two populations of PC could be formed during the reaction, bulk PC and PC covalently bounded to AL-NW. The product was removed from the reactor by dissolving in chloroform, and was recovered by precipitating into an excess of methanol. Phenol gathered at the end of the distillation system formed crystals on condenser and flask at room temperature.

Figure 4- 1 Experimental setup for in-situ polymerization of ALNW with BPA-PC

4.4 Melt phase polymerization of isosorbide and BPA copolymer nanocomposite

Composites of ALNW in pure isosorbide-PC and isosorbide/BPA PC compolymers were synthesized using melt phase polymerization procedures that were similar to the method used for pure BPA-PC.

Pure isosorbide-PC synthesis was tried initially, but the PC produced was not of high enough molecular weight to be precipitated. Copolymers with isosorbide/BPA ratios of
95/5, 75/25, and 50/50 were synthesized. And the 95/5 copolymer shows significantly high molecular weight compared to other copolymers. This was consistent with the work reported by Lee, who also proved that the 95/5 ratio copolymer exhibits the highest molecular weight among all the copolymer compositions [42]. The reason of the dependence between the molecular weight and monomer ratio will be studied in Chapter 6. In the synthesis work, Lee’s synthesis method and the monomer composition will be followed to produce AL-isosorbide-BPA-PC nanocomposites.

The copolymer of 95% isosorbide/5% BPA was used to produce composite with ALNW. For this reaction 1.46g isosorbide (10mmol), 0.144g bisphenol A (0.5mmol), 2.25g DPC (10.5 mmol), 0.115g ALNW and 0.7mg DMAP were added to a round bottom flask connected to a vacuum pump and condenser. The flask was heated to 187°C under nitrogen atmosphere for 1hour. The temperature was increased to 200°C and vacuum pump was turned on to facilitate the removal of phenol. After 1 hour the nitrogen inlet was stopped and the temperature was gradually increased to 250°C, and maintained between 250°C to 275°C for 2 hours. During the reaction, phenol was collected in the waste gathering flask connected to the condenser; polymer synthesized in the flask was recovered by dissolution in methylene chloride and precipitated into methanol. The product was filtered and dried in vacuum oven at 110°C for 1day.

4.5 Solid State Polymerization (SSP)

Solid state polymerization (SSP) was carried out to increase the molecular weight of PC oligomer synthesized using melt phase polymerization. The BPA-PC oligomer was maintained at 180°C, which is 3°C below the melting point of BPA-PC pre-polymer
reported in the literature, under continuous N₂ flow to sweep the byproduct phenol from the reactor. After 1 hr, the temperature was slowly increased by 5°C/hr, until the temperature reached 240°C; the reactor was maintained at 240°C for another 8 hr to ensure high molecular weight BPA-PC was achieved. Similar approaches were taken with isosorbide-PC, but significant increase in molecular weight was not observed.

4.6 Soxhlet extraction on nanocomposite

Soxhlet extraction was used to separate PC from the functionalized ALNW after in-situ polymerization. The solubility of bulk PC is limited in tetrahydrofuran (THF), and ALNW does not dissolve in THF at all. The experimental setup of Soxhlet extraction is shown in Figure 4-2.

In the Soxhlet extractor, the boiling flask was filled with about half the maximum volume of the extraction solvent. The boiling flask was connected to an extraction chamber, where AL-PC nanocomposites were kept. The powders were often placed in a thimble made from thick filter paper and then put into the chamber to avoid loss of ALNW. A condenser was connected to the extraction chamber to minimize the solvent loss from vaporization [6,58]. The extraction started when the boiling flask was heated to 90°C. After a while the solvent boiled to flood into the extraction chamber and dissolve the AL-PC nanocomposites. When the chamber was almost full, the solvent flowed back to the boiling flask through the Siphon arm. The whole process repeated for 24 hours to ensure the complete remove of bulk PC. After the two components were thoroughly separated, the extraction was stopped by turning off the heat. The functionalized ALNW was left in the thimble, and can be recovered and dried for future analysis. The bulk PC was totally dissolved in THF in the
boiling flask, and could be recovered by precipitating the solution into methanol, filtering, and drying in vacuum oven.

Figure 4-2 Experimental setup of Soxhlet extractor[57]
4.7 Solution Casting of Films

AL-PC nanocomposite obtained after SSP was diluted with high molecular weight BPA-PC purchased from Aldrich to produce composite with different ALNW weight concentrations. To make 1 film, 1.7g of the PC mixture was blended in the solution phase with 17 ml of methylene chloride. The solution was sonicated using ultrasonic cleaner (FS60, Fisher Scientific) for 30 minutes, mixed on a stir plate for 12 hours, and cast in a glass dish in a hood for 24 hours. The film was kept in a vacuum oven at 120°C for 12 hours to remove the residue solvent, whose boiling point is 36°C at 1 atm.

4.8 Transesterification polymerization kinetics measurement

The reaction kinetics and equilibrium behaviors of the isosorbide/BPA PC copolymers and homo-polymers were monitored using a modified method reported in the literature [13, 14]. Specifically the reaction was carried out in a closed flask as shown in Figure 4-3, to allow phenol to build up in the system. Literature indicated that the equilibrium of BPA-PC is at about 50%-60% of conversion rate for melt phase transesterification with DPC. Similar studies were performed for isosorbide with DPC and copolymer systems with different monomer ratios. Specifically, for BPA-PC, 10g BPA and 9.4g DPC were added to a 50mL round bottom flask. The flask was heated in an oil bath under nitrogen atmosphere, and 10mg catalyst, n-Butyltinoxidehydroxide, was added to the flask. The mixture was stirred with a magnetic stir bar. The addition of catalyst was considered the starting point of the transesterification reaction. Small amount of the melt phase was sampled from the reactor at different times during the reaction, immediately injected into small ampoules and quickly cooled down in
cold water. The isothermal kinetics measurements were typically performed for up to 100 minutes, and temperature up to 210 °C.

The same procedures were used for isosorbide/BPA copolymer and isosorbide-PC synthesis reaction kinetics study, with the molar ratio of total hydroxyl end-group over phenolic end group was always kept at 1. End group analysis and phenol composition were used to monitor the kinetics and equilibrium. Nuclear magnetic resonance was used for end group composition studies.

\[ \text{N}_2 \quad \rightarrow \quad n\text{-Butyltinoxidehydroxide} \]

Figure 4-3 Experimental setup of transesterification kinetics measurement

4.9 Characterization

4.9.1 Nuclear Magnetic Resonance (NMR)

Quantitative structure and end-group analysis of PC, and the reaction mixture taken from the reactor for transesterification kinetics measurement was carried out using Bruker Advance 600MHz Spectrometer in Department of Chemistry and Biochemistry instrument center. The molecular weight of PC oligomer was also determined using NMR end-group quantification as described in Chapter 5.
4.9.2 Fourier Transform Infrared Spectroscopy (FTIR)

In order to confirm the structure of PC synthesized from melt phase polymerization and the presence of covalent bound between the alumina nanowhisker and PC, the Varian Excalibur Series FTS-4000 Spectrometer and the UMA-600 Microscope were used.

4.9.3 Thermogravimetric analysis

TA Instruments Q50 Thermogravimetric Analyzer was used to identify degradation properties of AL-PC nanocomposites, as well as to determine the percentage of ALNW in the PC product. A ramp process from room temperature to 700°C at 5°C/min temperature gradient was used with nitrogen flow rate maintained as 40mL/min.

4.9.4 Differential Scanning Calorimeter

Thermal analysis is carried out using Perkin Elmer Diamond Differential Scanning Calorimeter. The test samples were dried under vacuum at 100°C for 12 hours. The dried samples were placed in aluminum pans and placed in DSC chambers under nitrogen flow. Glass transition temperature ($T_g$) can be calculated from the curves.

4.9.5 Tensile strength testing

An ASTM-638 type V standard die was used to cut the PC film samples. Because the films are not long enough, the entire dog-bone shaped die was not used. In this research, only the rectangular piece in the middle of the die was utilized. The lengths of the pieces ranged from 1.8 in to 2.0 in, and the width was 0.25in, following the standard. The rectangular strips were loaded in an Instron tensile tester in Polymer Institute, where a pre-load force ranged from 0.3 N to 1.0 N was applied. The stress exerted on the samples was at a strain rate of 1 in/min.
Chapter 5

Polycarbonate Synthesis and Characterization

In this chapter, the characterizations of AL-PC nanocomposites and isosorbide based polymers are shown. A structural-property study of thermal, mechanical, and structural property tests have been investigated.

5.1 AL-BPA-PC nanocomposites

The AL-BPA-PC nanocomposites produced through melt-phase in-situ polymerization were analyzed. The presence of covalent bond between the ALNW and polymer matrix will be confirmed by FTIR spectrum. The molecular weight of the AL-PC synthesized through melt phase transesterification and SSP will be calculated using NMR end group analysis. The impact of ANLW on thermal mechanical properties will be discussed.

5.1.1 Confirmation of backbone structure

In order to investigate the structure of the bulk PC and the presence of covalently bounded BPA-PC on ALNW surface, Soxhlet extraction with THF was used for 24h to isolate the bulk PC and the functionalized alumina nanowhisker from the PC nanocomposite synthesized using melt phase polymerization. FTIR spectra of the isolated alumina nanowhisker and bulk PC are given in Figure 5-1, along with the spectra for pure PC synthesized using the same method and raw alumina nanowhisker. The FTIR the
spectra of PC is consistent with spectra in literature[2]. The bulk PC (spectra C) from nanocomposites has the same peaks as pure PC (spectra B).

![FTIR spectra](image)

Figure 5-1 FTIR spectra of (A) functionalized alumina nanowhisker isolated from the PC nanocomposite, (B) pure PC synthesized using melt phase polymerization, (C) PC oligomer recovered from PC nanocomposite, and (D) raw alumina nanowhisker.

The peak assignment for the PC samples are listed in Table 5-1 and shown in Figure 5-1. The spectrum of B and C were identically the same, he polymer produced through in-situ polymerization was confirmed to be the same as melt phase polymerization. The significant peaks at 1497 cm\(^{-1}\) and 1508 cm\(^{-1}\) (peak 4 for aromatic ring) can be found in the functionalized alumina nanowhisker but not in the raw alumina. These two peaks are consistent with the peaks in both pure and extracted PC assigned to the aromatic ring stretching. Peak 5 for the recovered AL-NW is consistent with C-O-C stretching in PC,
and peak 6 can be attributed to the aromatic CH stretching with a small shift. As the nanowhiskers were washed thoroughly, the peaks can be attributed to the PC bounded to the surface of alumina nanowhisker. Similar methods were reported in earlier study by our group of AL-BPA-PC composites synthesized by solution based polymerization. [6]

Table 5-1 Absorbance bands for pure PC, PC oligomer isolated, raw alumina nanowhisker and functionalized alumina nanowhisker

<table>
<thead>
<tr>
<th>Band assignment</th>
<th>Functionalized alumina (cm⁻¹)</th>
<th>Pure PC(cm⁻¹)</th>
<th>PC oligomer(cm⁻¹)</th>
<th>Raw alumina(cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>OH stretching (1)</td>
<td>3300</td>
<td>3480</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CH stretching (2)</td>
<td>2962</td>
<td>2962</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C = O stretching(3)</td>
<td>1786</td>
<td>1770</td>
<td>1770</td>
<td></td>
</tr>
<tr>
<td>Aromatic ring (4)</td>
<td>1497</td>
<td>1497</td>
<td>1497</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1508</td>
<td>1508</td>
<td>1508</td>
<td></td>
</tr>
<tr>
<td>C -O -C stretching(5)</td>
<td>1257</td>
<td>1276-1120</td>
<td>1276-1120</td>
<td></td>
</tr>
<tr>
<td>Aromatic CH(6)</td>
<td>1076</td>
<td>1080&amp;1014</td>
<td>1080&amp;1014</td>
<td></td>
</tr>
</tbody>
</table>

5.1.2 Molecular weight calculation using NMR Analysis

Molecular weight of the bulk BPA-PC recovered from the nanocomposite following melt phase polymerization and solid state polymerization (SSP) was analyzed by NMR end group quantification method developed by Kim et. al[59]. The structure and carbon assignment of BPA-PC synthesized by melt phase and solid state polymerization are shown in Figure 5-2.

Figure 5-2 Carbon assignment and structure of BPA-PC synthesized by transesterification polymerization [59]
Carbons numbered 1-4 are assigned to aromatic ring structure of PC repeat unit. Number 8-11 are assigned to aromatic ring structure of phenyl end group. Number 1’-4’ and 1”-4” aromatic are carbon atoms from hydroxyl end group. For this method, the peak area of C nuclear 10 was used for the phenyl of DPC, and C nuclear 3 was used for the BPA in the repeat unit. In order to calculate the molecular weight of the PC following melt phase or solid state polymerization, the number of phenyl end group and hydroxyl end group per repeat unit were calculated by Equation 5-1.

Number of phenyl end group per repeat unit = \frac{\text{peak area of 10}}{2 \times (\text{peak area of 3})} = n_1 \quad \text{(Equation 5-1)}

The ratios of hydroxyl end groups to number of repeat unit was determined using Equation 5-2 where carbon 5’ was central C of BPA with OH end group and carbon 5 is central carbon of BPA in repeat unit. The number of repeat units can be determined from Equation 5-3 and the ratio of end group to repeat units found in Equation 5-1, and 5-2.

Number of hydroxyl end group per repeat unit = \frac{\text{carbon 5’ peak area}}{\text{carbon 5 peak area}} = n_2 \quad \text{(Equation 5-2)}

Number of repeat unit = \frac{2}{(n_1 + n_2)} = n_r \quad \text{(Equation 5-3)}

And number average molecular weight can be calculated by

\[
M_n = n_r \times (n_1 \times 121 + n_2 \times 227 + 254) \quad \text{(Equation 5-4)}
\]

Where 121, 227 and 254 are molecular weight of phenyl end group, hydroxyl end group, and a repeat unit as shown in Figure 5-2.

\(^{13}\)C NMR spectra of bulk BPA-PC recovered from nanocomposites after melt phase synthesis and recovered after different degree of SSP are shown in Figure 5-3 and 5-4.
Figure 5-3 NMR spectra of bulk PC from PC nanocomposite after melt state polymerization

And the chemical shifts for the bulk BPA-PC peaks were shown in Table 5-2, all the peak locations are consistent with the literature reported by Kim. [59]
Table 5-2 $^{13}$C NMR chemical shifts for BPA-PC [59]

<table>
<thead>
<tr>
<th>Peak assignment</th>
<th>Chemical shift (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>7</td>
<td>152.56</td>
</tr>
<tr>
<td>8</td>
<td>150.96</td>
</tr>
<tr>
<td>1</td>
<td>148.94</td>
</tr>
<tr>
<td>4</td>
<td>148.42</td>
</tr>
<tr>
<td>10</td>
<td>129.53</td>
</tr>
<tr>
<td>3</td>
<td>128.03</td>
</tr>
<tr>
<td>3''</td>
<td>127.81</td>
</tr>
<tr>
<td>11</td>
<td>126.4</td>
</tr>
<tr>
<td>9</td>
<td>120.91</td>
</tr>
<tr>
<td>2</td>
<td>120.42</td>
</tr>
<tr>
<td>2'</td>
<td>120.22</td>
</tr>
<tr>
<td>2''</td>
<td>114.96</td>
</tr>
<tr>
<td>5</td>
<td>42.55</td>
</tr>
<tr>
<td>5'</td>
<td>42.08</td>
</tr>
</tbody>
</table>

In Figure 5-3, peak 7-10 represent carbon provided by phenolic end group, 1-5 are carbons from repeat unit. 5’ is the central carbon from hydroxyl end group. Peak 1’-4’ were not observed in this figure because those peaks were close to the repeat unit peaks 1-4. Under current resolution, peak 1’-4 are hard to identify. Only peak 5’ is well separated from peak 5. So in this research, the ratio of peak 5’ over peak 5 was chosen to determine the number of phenolic end group per repeat unit.
Figure 5-4 NMR spectra of bulk PC from PC nanocomposite following solid state polymerization at (a) 200°C, (b) 220°C, and (c) 240°C.

As shown in Figure 5-3 and 5-4, there are visible peaks for both the BPA and DPC end groups at 5’ and 7-10 which indicates that low molecular weight PC was produced after
this step similar results were seen following SSP at 200°C as shown in Figure 5-4(a).

As the SSP temperature was increased, the peaks for end group carbons were all smaller as shown in Figure 5-4. For example, all of the peaks of end group carbons are too small to be seen in the spectra following SSP at 240 °C (Figure 5-4 (c)). This indicates that the chain length of PC in the nanocomposites was increasing as the SSP temperature increases. End group and molecular weight calculation of the samples following melt phase polymerization an SSP are listed in Table 5-2.

Table 5- 2 Molecular weight and end group analyze of Al-PC after different SSP stages

<table>
<thead>
<tr>
<th>Number of repeat unit</th>
<th>Hydroxyl end group/phenyl end group</th>
<th>Mn</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al-PC melt phase</td>
<td>13</td>
<td>0.6</td>
</tr>
<tr>
<td>Al-PC SSP 200 °C</td>
<td>17</td>
<td>1.1</td>
</tr>
<tr>
<td>for 2hr</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Al-PC SSP 220 °C</td>
<td>21</td>
<td>0.8</td>
</tr>
<tr>
<td>for 2hr</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Al-PC SSP 240 °C</td>
<td>&gt;50</td>
<td></td>
</tr>
<tr>
<td>for 8hr</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

As SSP progressed, the chain length of bulk polymer increases; and BPA-PC nanocomposites with increased molecular weight can be recovered. After 8 hours of SSP at 240°C the polymer chain was long enough that the ratio of end group over repeat unit is too low to measure, since the signal of the carbon peaks from end group is too weak and cannot be observed using this NMR 13C end group analyze method. According to Kim’s work, this end group calculation method met its limitation when the number of repeat was higher than 50. So it can be assumed that, the molecular weight of AL-BPA-PC produced after SSP at 240°C for 8 hours was more than 10,000. Other analysis
methods such as gel permeation chromatography (GPC) or MALDI-TOF could be used in the future work to determine the molecular weight of the bulk BPA-PC with high molecular weight. MALDI-TOF was tried at initially, but the because of the equipment limitation, the measurement range was limited to 20 repeat units.

5.1.3 Thermal analysis

Thermal gravimetric analysis was carried out to study the effect of SSP and addition of AL-NW on the thermal stability of BPA-PC produced using melt phase polymerization. Figure 5-5 shows the weight loss of PC (PC melt phase and PC SSP 240) and 5% aluminum PC nanocomposite (Al-PC melt phase and before and after SSP during heating from room temperature to 700°C at 5°C/min under N₂ atmosphere. In Figure 5-6, the weight loss of original ALNW and functionalized ALNW isolated from the AL-BPA-PC nanocomposite using Soxhlet extraction during heating from room temperature to 1000°C at 5°C/min under N₂ atmosphere is shown. Figure 5-7 is the derivative weight loss of the BPA-PC samples. In Figure 5-8, the derivative weigh loss curve of functionalized ALNW is compared with the curve of BPA-PC. The onset temperature of weight loss is defined as the temperature at which there is a 5% weight loss of the sample [11]. The weight loss onset temperature, maximum derivative weight loss and residue weight loss at 650°C, at which the degradation is considered to be completed in the literature[11, 60], are listed in Table 5-3.
Figure 5- 5 Weight loss of BPA-PC and AL-BPA-PC nanocomposite following melt phase polymerization and after SSP at 240°C in nitrogen atmosphere at 5°C/min
Figure 5-6 Weight loss of (a) raw ALNW, and (b) functionalized ALNW isolated from AL-BPA-PC nanocomposite in nitrogen atmosphere at 5°C/min
Table 5- 3 Thermal stability analysis of PC and 5% aluminum PC nanocomposite

<table>
<thead>
<tr>
<th></th>
<th>Weight loss onset temperature</th>
<th>Maximum deriv. weight loss temperature</th>
<th>Residue weight at 650°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>PC melt phase</td>
<td>452°C</td>
<td>563°C</td>
<td>20%</td>
</tr>
<tr>
<td>PC SSP 240</td>
<td>482°C</td>
<td>563°C</td>
<td>20%</td>
</tr>
<tr>
<td>Al-PC melt phase</td>
<td>429°C</td>
<td>579°C</td>
<td>25%</td>
</tr>
<tr>
<td>Al-PC SSP 240</td>
<td>443°C</td>
<td>579°C</td>
<td>25%</td>
</tr>
<tr>
<td>Functionalized</td>
<td></td>
<td>224°C &amp; 440°C</td>
<td>67%</td>
</tr>
<tr>
<td>ALNW</td>
<td>230°C</td>
<td>224°C</td>
<td>71%</td>
</tr>
</tbody>
</table>

Figure 5-7 Derivative weight change of PC and PC nanocomposite before and after SSP at 240°C at 5°C/min
The residue weight percentage after heating can be used to confirm the AL-PC nanocomposite composition. The weight loss of ALNW at 650°C was 29%, and pure PC was 80%. Given the weight loss of base AL-PC was 75%, the percentage of AL in the AL-PC can be estimated as 5.2%, which is similar to the feed ratio. Therefore, the ALNW loading in the synthesis batch was confirmed.

The difference between the residue weight of raw ALNW and functionalized ALNW, and the small derivative weight loss peak at 440°C together proved that after in-situ polymerization, part of PC chains were bonded to the ALNW surface. According to the residue weight loss, the composition of BPA-PC in the functionalized ALNW is 8% by
weight.

The onset weight loss temperature of 5% for the aluminum nanocomposites were lower than that of pure BPA-PC. This may be because of the sharp weight loss of alumina oxide at 200°C, not because of the degradation of PC. For pure BPA-PC and AL-BPA-PC with 5% nanowhiskers solid state polymerization resulted in increasing the onset temperature by 20-30°C.

As shown in Figure 5-7, the maximum weight loss peak was not affected by the increase in molecular weight following SSP. Following addition of 5 wt% of aluminum nanowhiskers, the width of the peak is narrow, and the max derivative weight temperature is 16°C higher than that of pure BPA-PC. Both pure BPA-PC and BPA-PC nanocomposites following SSP showed significant increase of the heat resistance compared to the literature, in which, the max weight loss temperature of pure PC (Makrolon 2805, Mn=15,100 ) was reported as 528°C[11].

5.1.4 Tensile Test

The AL-BPA-PC nanocomposites produced through in-situ polymerization and SSP were diluted from 5% weight percent of ALNW to 0.5%, 0.7%, 1%, 1.5%, and 2% using BPA-PC purchased from Sigma Aldrich with a molecular weight of Mn= 64000. The films were produced using solution casting from methylene chloride and thoroughly dried. Note that the molecular weight measured via NMR of the bulk BPA-PC following SSP was greater than 10,000, as shown in Table 5-2. The pure BPA-PC film was produced using BPA-PC purchased from Sigma Aldrich to allow a comparison with composites produced through solution based polymerization by our group [6].
The tensile properties of these AL-PC nanocomposite films were tested. For each ALNW loading, three films were tested, and the final results were taken as average value of the three films. Because of the difference between the high molecular weight PC used for the film casting. The results were normalized to be easy to compare. The normalized tensile strength at yield for nanocomposite as a function of ALNW concentration are present in Figure 5-9. And the normalized Young’s modulus as function of ALNW concentration in BPA-PC are shown in Figure 5-10.

Figure 5-9 Normalized tensile strength at yield as a function of ALNW loading for AL-BPA-PC synthesized through (∗)melt phase in-situ polymerization, (□)solution based in-situ polymerization at room temperature[6], and (Δ) without in-situ polymerization[6] with a strain rate of 1in/min
Figure 5- 10 Normalized Young’s modulus as a function of ALNW loading for AL-BPA-PC synthesized through (●)melt phase in-situ polymerization, (□)solution based in-situ polymerization at room temperature[6], and (∆) without in-situ polymerization[6] with a strain rate of 1in/min.

As shown in Figure 5-9 and 5-10 AL-BPA-PC synthesized through melt phase polymerization and SSP with all loadings exhibited increase in tensile strength and Young’s modulus relative to pure BPA-PC at all loadings.

The mechanical properties of AL-BPA-PC synthesized through melt phase and SSP were compared to the previous work done by our group in Figure 5-9 and 5-10, where the AL-BPA-PC with same range of ALNW loading were synthesized through solution based in-situ polymerization.

The difference in outcomes may be due to the fact that in lab scale melt phase polymerization, the mixing was not as good as in the solution based polymerization would limit molecular weight of bulk PC. In the melt phase, the viscosity of the reactant
mixture is getting higher and higher as the temperature raised. The ALNW added during the polymerization may not be well dispersed in the reactant mixture, which caused uneven functionalization of the ALNW and short PC chain on the nanowhiskers surface. Further studies may be focused on upgrading the melt phase polymerization reactor with more powerful mixer to achieve higher degree of mixing. This may allow improved functionalization and dispersion of ALNW.

5.2 Isosorbide-PC isosorbide/BPA copolymer and nanocomposite

95% isosorbide/5% BPA copolymer synthesized through melt phase polymerization was analyzed by FTIR to confirm the structure. This section discussed the synthesis and characterization of isosorbide copolymer composites

5.2.1 FTIR analysis

The structure of isosorbide and BPA copolymer are shown in Figure 5-11.

![Figure 5-11 Structure of Isosorbide/PC copolymer](image)

FTIR spectrum of isosorbide-BPA copolymer is shown in Figure 5-12, with peak assignment listed in Table 5-4. The copolymer (curve c) exhibits the presence of polycarbonate bond, but the peaks of aromatic rings (peak 5) were not significant, this is because of concentration of BPA in the monomer feed ratio is only 5%. The characteristic OH stretching of isosorbide peak 1 was not observed in the copolymer, because in polymer structure it only occurs in limited amount as end groups. This is consistent with high Mw
needed for this project. The appearance of C = O stretching at 1770 cm\(^{-1}\) (peak 3) in copolymer is attributed to transesterification reaction with DPC. These identical peaks are consistent with IR data of isosorbide PC in literature.

Table 5-4 Absorbance bands for FTIR spectra of isosorbide/BPA copolymer, isosorbide monomer, and BPA-PC

<table>
<thead>
<tr>
<th>Peak number</th>
<th>Assignment</th>
<th>Purified isosorbide (cm(^{-1}))</th>
<th>BPA-PC (cm(^{-1}))</th>
<th>5%BPA copolymer (cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>OH stretching</td>
<td>3360</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>CH stretching</td>
<td>2951 &amp; 2877</td>
<td>2962</td>
<td>2962 &amp; 2862</td>
</tr>
<tr>
<td>3</td>
<td>C = O stretching</td>
<td>1770</td>
<td></td>
<td>1770</td>
</tr>
<tr>
<td>4</td>
<td>Aromatic ring</td>
<td>1497</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>C-O-C stretching</td>
<td>1276-1120</td>
<td>1315-1137</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>Aromatic CH</td>
<td>1080 &amp; 1014</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Figure 5-12 FTIR spectra of (a) purified isosorbide monomer, (b) BPA-PC synthesized through melt phase polymerization (c) 5%BPA-95% isosorbide copolymer
AL-BPA-isosorbide-PC nanocomposites with an isosorbide/BPA ratio of 20:1 was synthesized using melt phase in-situ polymerization. Bulk 5%BPA-95%isosorbide-PC was extracted from the nanocomposite by Soxhlet extraction using a mixture of chloroform and THF as the solvent for 24 h. The extracted AL-NW and bulk PC recovered from the solution were dried overnight in a vacuum oven. The FTIR spectra of the functionalized AL-NW is compared with raw alumina and isosorbide PC in Figure 5-13. There are peaks associated with isosorbide-PC on the spectra of the functionalized alumina nanowhiskers (peak 3, 4). The peak assignments are listed in Table 5-5. Because the alumina nanowhiskers were washed thoroughly, the appearance of the peaks associated to BPA-isosorbide-PC are due to the bonded PC chains on alumina surface.

Figure 5- 13 FTIR spectra of (a) alumina nanowhiskers (b) alumina nanowhiskers extracted from in-situ AL-BPA-isosorbide-PC nanocomposite (c) BPA-isosorbide-PC recovered from soxhlet extraction
Table 5- 5 Absorbance bands for FTIR spectra of ALNW, ALNWextracted from in-situ AL-BPA-isosorbide-PC nanocomposite, and BPA-isosorbide-PC recovered from soxhlet extraction

<table>
<thead>
<tr>
<th>Peak number</th>
<th>Assignment</th>
<th>Raw ALNW (cm(^{-1}))</th>
<th>Functionalized alumina(cm(^{-1}))</th>
<th>Isosorbide and BPA copolymer(cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>OH streching</td>
<td>2000-3670</td>
<td>3000-3670</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>CH streching</td>
<td>2951&amp;2877</td>
<td></td>
<td>2962&amp;2862</td>
</tr>
<tr>
<td>3</td>
<td>C = O streching</td>
<td>1770</td>
<td></td>
<td>1770</td>
</tr>
<tr>
<td>4</td>
<td>C-O-C streching</td>
<td>1180-1300</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

5.2.2 Glass transition temperature measurement

The 95%isosorbide/5%BPA copolymer synthesized through melt phase polymerization was dissolved in chloroform, precipitate into methanol, and dried in a vacuum oven at 100 °C for 12 hr. The glass transition temperature of the copolymer was analyzed using DCS. The sample was heated from room temperature to 300 °C at a rate of 25 °C/min, after the first heating, thermal history was removed, the second heating curve was analyzed in Figure 5-14 to calculate \( T_g \).
Figure 5-14 Second heating DSC curve of 5%BPA-95%isosorbide copolymer at a rate of 25 °C/min

Read from Figure 5-13, the T_g of the 5%BPA-95%isosorbide copolymer was 153 °C. This T_g is in same range as values reported in literature and shown in table 3-3 and 3-3. The T_g of Lexan BPA-PC was reported as 145 °C[61], compared to the BPA/isosorbide copolymer, an increase was observed. This is consistent with the more rigid structure of isosorbide compared to BPA.

5.2.3 Thermal gravimetric analysis

Thermal gravimetric analysis of the 95%isosorbide-5%BPA copolymer was analyzed using TGA, and compared with the the 100%BPA-PC, and 100% isosorbide-PC. The samples were heated from room temperature to 600 °C at 5 °C/min under nitrogen atmosphere. The curves of derivative weight loss are shown in Figure 5-14.
Figure 5- 15 Derivative weight change curves of 100% BPA-PC, 100% isosorbide-PC, and 5%BPA-95isosorbide-PC under nitrogen atmosphere at 5°C/min

<table>
<thead>
<tr>
<th>Material</th>
<th>Maximum deriv. weight loss temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>5%BPA/95%isosorbide</td>
<td>350°C &amp; 470°C</td>
</tr>
<tr>
<td>100% isosorbide-PC</td>
<td>364°C</td>
</tr>
<tr>
<td>100%BPA-PC</td>
<td>563°C</td>
</tr>
</tbody>
</table>
It can be observed that there is only one derivative weight loss peak for pure isosorbide-PC and pure BPA-PC. For the copolymer, one large peak can be seen at 350 °C, which is close to the peak of 100%isosorbide-PC, and a small peak can be found at 470 °C, which is close to the peak of 100% BPA-PC. The difference in the peak area is consistent with the fact that the feeding ratio of the monomers was BPA/isosorbide= 5/95.

The two peaks found in the derivative weight loss curves proved that a copolymer of isosorbide and BPA was successfully synthesized through the melt phase polymerization.

5.3 Summary

In this chapter structural, thermal, and mechanical properties of the AL-BPA-PC nanocomposites and AL-isosorbide-BPA-PC nanocomposites were studied.

In-situ polymerization was confirmed by the FTIR assignments. The peaks standing for the functional group of BPA appealed on the functionalized ANNW proved that polymer chains were growing on the surface of the ANLW.

NMR end group analysis was used to calculate molecular weight of the bulk BPA-PC recovered following in-situ polymerization the molecular weight of AL-BPA-PC was successfully upgraded using SSP.

The TGA analysis showed that SSP improved the heat resistance of both BPA-PC and AL-BPA-PC nanocomposites. The addition of ALNW also increased the maximum derivative weight loss temperature.

Compared to BPA-PC, AL-BPA-PC synthesized through in-situ polymerization with concentrations between 0.5%- 2% all showed enhanced tensile properties. Both tensile strength at yield and Young’s modulus were improved following addition of ALNW to
polycarbonates. However, the tensile strength and Young’s modulus did not increase continuously as the ALNW loading increased. This might be caused by insufficient mixing at the melt phase polymerization process.

Isosorbide and BPA copolymer with an isosorbide/BPA molar ratio equals 95/5 was observed to have the highest molecular weight among all other compositions under the same reaction conditions. AL-isosorbide-BPA-PC nanocomposites were chosen to synthesize. The presence of the covalent bond between the functional ALNW and copolymer chain was proved by FTIR spectra similar as the AL-BPA-PC. The possibility of in-situ polymerize isosorbide dominated copolymer at melt phase was proved. The glass transition temperature of the 5%BPA/95%isosorbide copolymer was measured through DSC. The value of $T_g$ suggested the molecular weight of the copolymer should be around 10,000.
Chapter 6

Transesterification Kinetics Study

Although the study of isosorbide transesterification with DPC has been investigated. The study of the reaction kinetics is still quite limited. An understanding of reaction kinetics plays a very important part when an optimization of the reaction was required to upgrade the molecular weight.

In this chapter, a method used to study the transesterification of BPA and DPC was modified for use with the isosorbide based PC copolymers. After the reliability of this model is verified, reaction rate constant were calculated for homo-polymer and copolymer synthesis reactions of isosorbide and BPA at different temperatures. The equilibrium kinetics were studied. Finally, a model was developed to simulate the time dependent concentration of homo and copolymers of isosorbide and BPA using data of homo-polymers. Suggestions on synthesis method optimization of synthesis conditions will be made based on the kinetics study.
6.1 Kinetics Model

The transesterification reaction of BPA with DPC, and ISO with DPC are shown in scheme 6-1 and 6-2, in terms of end group and growing chain. Inherently, these 2 reactions can both be expressed in terms of end group is:

\[ A + B \rightleftharpoons C + P \]

Where A represents hydroxyl end group of BPA, B is phenolic end group from DPC, C is PC chain, and P is phenol.

It was reported in the literature that the forward reaction is a first order reaction with respect to BPA and DPC respectively. If the amount of hydroxyl groups and phenyl groups are assumed to be equal at all the times during the reaction, and the reactivity of
end group is not affected by chain length. The reaction becomes a second order reaction in terms of concentration of hydroxyl end group \([A]\), or phenol concentration \([P]\). For second order reaction, the rate expression for batch reactor can be integrated to find \(k\).

The method reported by Ignatov[14] was modified here. The explanations used to determine the rate kinetics are shown as:

\[ [A]_0 - [A] = [B]_0 - [B] \]

\[ [A]_0 = [B]_0 \]

Where \([A]_0\) and \([B]_0\) are the feed concentration of A and B to reactor. Since \([A]_i\) and \([B]_i\) at any time during the reaction were equal at any time. The reaction expressing can be specified to

\[ r = k \cdot C_A \cdot C_B \]
\[ r = k \cdot C_A^2 \]

and it can be integrated into

\[ k \cdot t = \frac{1}{[A]_i^2} - \frac{1}{[A]_0^2} \quad (6-1) \]

Since the concentration of phenol \([P]\) can be determined from concentrations of hydroxyl end groups

\[ [P] = [A]_0 - [A]_i \]

So the equation can also be expressed as

\[ k \cdot t = \frac{[P]}{[A]_0^2 - [P][A]} \quad (6-2) \]

By potting \(1/[A]_i-1/[A]_0\) versus time, the effective reaction rate can be obtained as the slope of linear fit of the data points. The effective rate constant can be also determined using phenol concentration by plotting \(\frac{[P]}{[A]_0^2 - [P][A]}\) over time. Since the concentration of
catalyst was constant, the reaction rate constant can be expressed as

\[ k = k^*/[\text{Catalyst}] \]

Hydroxyl end group concentration \([A]\) and phenol concentration \([P]\) will be used to independently determine the rate kinetics for BPA-PC. The method with the phenol will be extended to isosorbide based PC and composites.

### 6.2 Experimental data analysis

To measure \([A]\) and \([P]\) values at different times during the reaction at regular intervals. Samples were taken following the procedures described in Chapter 4. The samples were dissolved in D-chloroform and analyzed by Bruker Advance 600MHz Spectrometer \(^{13}\text{C}\) NMR spectra. An example of the peak assignments of the spectra were shown in Figure 6-1.
According to Kim's work [59], the peak assignments of BPA-PC synthesis mixture $^{13}$C NMR spectra peak assignment are shown in Figure 6-1. The central carbon on isopropyl of BPA: unreacted, single end group reacted, and both end group reacted BPA in the mixture were assigned as 5B, 5' and 5 respectively. The ratio of unreacted hydroxyl end groups to total end groups will be designed as A% and can be expressed as
\[ A_i\% = \frac{Unreacted\ end\ group}{Total\ end\ group} \]

And A\% can be determined using peak area from NMR as

\[ A_i\% = \frac{\frac{5'value\ peak\ area}{2} + 5B\ peak\ area}{5 + 5'value + 5B\ peak\ area} \tag{6-3} \]

\[ [A]_i = A_i\% [A]_0 \tag{6-4} \]

In Figure 6-1 (b), the same phenolic carbon provided by phenol and DPC were assigned as 2P and 2D. The ratio of phenol to total amount of carbonyl end groups can be expressed as

\[ P\% = \frac{Phenol\ end\ group}{Phenol\ end\ group + Phenol} \]

The peak assignment for 2D from DPC is at 121.07ppm, and the 2D from single end group reacted DPC is at 120.91ppm. The difference between the peak locations is too small to make them totally separated. Therefore, the amount of unreacted DPC end group was considered as the total area of the two peaks labeled at 2D.

\[ P\% = \frac{2P\ peak\ area}{2D + 2P\ peak\ area} \tag{6-5} \]

\[ [P] = P\%[B]_0 \tag{6-6} \]

The rate constant for BPA-PC polymerization kinetics study can be determined using both [P] an [A]i. If the k value calculated using the two concentrations are consistent, the reliability of the phenol method is confirmed. For isosorbide-PC polymerization, the peak assignment of isosorbide-PC has not been fully studied. Since phenolic end group of DPC is the only source of benzene ring of phenol, equation (2) and value of [P] can also be used to calculate the k value.
Figure 6-2 Kinetics curve of BPA and DPC transesterification polymerization at 165 °C calculated based on a: Equation (6-1), b: Equation (6-2)

The [A] and [P] values at different times were measured using $^{13}$C NMR plotted versus time. The linear fitting of the data points were taken as the kinetics curve of the
polymerization at the certain temperature. The slope of the linear fitting is the effective rate constant, which is $k^*$ described in Equation (6-1) and (6-2). An example of the kinetics curve was shown in Figure 6-2. Figure 6-2(a) is kinetics curve calculated using BPA hydroxyl group concentrations as a function of time and substitute into Equation (6-1), Figure 6-2 (b) is kinetics curve determined using phenol concentration and substituted into Equation (6-2). For both of the curves, a linear trend line fits to the data to determine the value of $k^*$ can be drawn.

6.3 Reaction rate constant of reaction kinetics

The method described in section 6-2 was used to monitor kinetics and equilibrium of isosorbide/BPA-PC copolymer and nanocomposites. Both the concentrations of unreacted hydroxyl group and phenol was used to determine rate constant for BPA-PC and nanocomposites synthesis as function of temperature. The phenol concentration was used to monitor the rate kinetics for isosorbide based polymer and copolymer.

The effective reaction rate of transesterification polymerization has shown to be affected by both temperature and catalyst. In this research, the catalyst and catalyst concentration were set as constant, with only the effect of temperature was studied.

6.3.1 BPA-PC

Kinetics studies of BPA and DPC transesterification were performed at 165°C, 190°C and 210°C. Using the linear fitting discussed in the previous section, the kinetics curves determined using Equation (6-1) were shown in Figure 6-3 (a), and curves determined using Equation (6-2) in Figure 6-3(b).
The effect of reaction temperature on the BPA-PC kinetics are shown in Figure 6-3 for the transesterification of BPA and DPC at different temperatures with a concentration of n-Butyltinoxidehydroxide is $2.6 \times 10^{-6}$ mol/mL.
BPA hydroxyl group (6-3a), and phenol concentration (6-3b). From both 6-3 (a) and 6-3(b), it was observed that for each reaction temperature, a well fitted linear fitting can be drawn through the data points. These results are consisted with second reaction and reported in literature for BPA-PC[52]. The slope of the curve is the effective rate constant that are normalized for catalyst concentration.

The rate constants calculated using kinetics data in Figure 6-3 from unreacted BPA hydroxyl end groups (k_{(1)}) and phenol concentration (k_{(2)}) are given in Table 6-1. For each k value, three samples were analyzed, and an average value was taken as the result.

<table>
<thead>
<tr>
<th>T(°C)</th>
<th>k_{(1)}/(10^{-6} \text{ mL}^2/\text{mol}^2 \text{ min})</th>
<th>k_{(2)}/(10^{-6} \text{ mL}^2/\text{mol}^2 \text{ min})</th>
</tr>
</thead>
<tbody>
<tr>
<td>165</td>
<td>1.4 ± 0.05</td>
<td>1.4 ± 0.04</td>
</tr>
<tr>
<td>190</td>
<td>4.4 ± 0.1</td>
<td>4.4 ± 0.1</td>
</tr>
<tr>
<td>210</td>
<td>10.6 ± 0.4</td>
<td>10.6 ± 0.4</td>
</tr>
</tbody>
</table>

As shown in Table 6-1, the rate constant determined using the two different components (hydroxyl and phenol) are consistent. Therefore, the buildup of phenol concentration in reactor can be used to monitor reaction kinetics for the isosoribde-PC and copolymer synthesized.

It was observed that as the temperature increased, there was an increase in rate constant. These results confirmed the assumptions of first order kinetics for the transesterification reaction reported in literature. In addition, the results for kinetics studies using phenol
concentration are consistent with those of hydroxyl end group of BPA and can be used for study with isosorbide based copolymers.

6.3.2 Isosorbide-PC

The reaction was applied to determine rate constant for isosorbide-PC. Because the peaks for isosorbide hydroxyl end group for different forms of isosorbide do not exhibit significant shifts, the phenol concentration was used to determine rate kinetics. The normalized rate expression for Equation 6-2 is given for isosorbide-PC in Figure 6-4(a) and rate constant in Table 6-2 as \( k_{ISO} \).

A similar study was performed for copolymer with equal molar feed of BPA and isosorbide, as shown in Figure 6-4(b). And the k value of the copolymerization were also reported in Table 6-2 as \( k_{50\%} \).

As shown in Figure 6-4, well fitted linear fittings were drawn through the data points. The slope of the linear fittings increased as the temperature increased.
Figure 6-4 Kinetics curve of transesterification of (a) isosorbide-PC, and (b) 50%BPA-50% isosorbide at different temperatures with a concentration of n-Butyltinoxidehydroxide is $2.6 \times 10^{-6}$ mol/mL.
Table 6-2 Rate constant of isosorbide transesterification with DPC, and 50% BPA-50% isosorbide copolymerization at different temperatures

<table>
<thead>
<tr>
<th>T(°C)</th>
<th>k_{ISO}/(10^{-6} \text{ mL}^2/\text{mol}^2 \text{ min})</th>
<th>k_{50%}/(10^{-6} \text{ mL}^2/\text{mol}^2 \text{ min})</th>
</tr>
</thead>
<tbody>
<tr>
<td>165</td>
<td>0.24 ± 0.005</td>
<td>0.33 ± 0.02</td>
</tr>
<tr>
<td>190</td>
<td>2.1 ± 0.2</td>
<td>1.9 ± 0.02</td>
</tr>
<tr>
<td>210</td>
<td>8.0 ± 0.9</td>
<td>4.3 ± 0.03</td>
</tr>
</tbody>
</table>

6.3.3 Temperature Dependence

The temperature dependent reaction rate data and rate constants were described for BPA-PC; isosorbide-PC and a 50/50 copolymer in previous sections. The reaction is an activated process that is typically described using Arrhenius relation in Equation 6-7

$$k = k_0 e^{-\frac{E_a}{RT}}$$

(6-7)

where $k_0$ is the prefactor, $E_a$ is the activation energy, R is the universal gas constant.
Figure 6-5 Arrhenius plot of 100% BPA transesterification with DPC, 100% isosorbide transesterification with DPC, and 50% BPA-50% isosorbide transesterification with DPC

Table 6-3 Values of prefactor and activation energy in Arrhenius equation for BPA-PC transesterification reaction; isosorbide-PC transesterification reaction; and 50%BPA-50% isosorbide copolymerization

<table>
<thead>
<tr>
<th></th>
<th>$E_a$ (kJ/mol)</th>
<th>$k_0$ (L$^2$/mol² min))</th>
</tr>
</thead>
<tbody>
<tr>
<td>BPA-PC</td>
<td>-77700± 7800</td>
<td>$2.6 \pm 0.16 \times 10^{15}$</td>
</tr>
<tr>
<td>Isosorbide-PC</td>
<td>-137200± 14000</td>
<td>$5.7 \pm 0.23 \times 10^{21}$</td>
</tr>
<tr>
<td>50%BPA-50%isosorbide-PC</td>
<td>-102200± 1020</td>
<td>$5.5 \pm 0.22 \times 10^{17}$</td>
</tr>
</tbody>
</table>
The plot plots for the polycarbonates shown in Figure 6-4 indicates a linear relationship between \( \ln(k) \) and inverse temperature \((1/T)\), which is consistent with Arrhenius equation. The values of \( E_a \) and \( k_0 \) are given in Table 6-3.

The temperature dependence of the isosorbide-PC is considerably sharper than the BPA-PC. The corresponding activation energy was largest for the isosorbide-PC with the lowest values for BPA-PC.

The reaction rate constant of 100% isosorbide is very small compared to 100% BPA at 165 °C, but as temperature increases, the two \( k \) values become more and more compatible, and finally the \( k \) value of 100% BPA and 100% isosorbide are almost equal to each other at 210 °C. For temperature greater than 210 °C, the rate constant of 100% isosorbide should exceed that of the 100% BPA.

For the equal molar copolymer, both the activation energy and the rate constant temperatures were observed to be in the middle of the two homo-polymerizations. An understanding of temperature dependence of kinetics is very important when designing the polymerization conditions. Industrially, 165 °C was chosen as the starting temperature of BPA transesterification, with a slow increase in temperature up to 260 °C. But for isosorbide, the same operating conditions may not be effective. At 165 °C, the \( k \) value of 100% isosorbide-PC was too small. Experimentally, around 190 °C will be more appropriate for the polymerization starting temperature, with gradually increase the temperature to 260 °C. Structurally, both the isosorbide and BPA both have a rigid ring structure, however there is no propylene structure providing flexibility to isosorbide. So the mobility of isosorbide will be restricted, a higher final temperature might be required.
to obtain PC with high molecular weight to overcome those effects.

The composition and reaction kinetics of monomers can have a significant effect on the nature of copolymers. The relative reactivity of monomers (BPA and isosorbide) can be modified by changing reaction temperature to produce random or block copolymers. For example, for a 50/50 BPA/isosorbide feed, at low temperature, the rate constant for BPA is much larger than isosorbide, so that oligomer would initially of high BPA-PC concentration than isosorbide-PC. At extreme, the sample would consist of large block of BPA-PC with interspersed isosorbide-PC units. As the concentration of BPA decreased, isosorbide-PC would be formed, producing a BPA-PC/ Isosorbide-PC block copolymer.

In summary, in this section, the effect of temperature on reaction kinetics was investigated. The transesterification of isosorbide is highly temperature dependent, the activation energy of isosorbide-PC was 1.8 greater than that of BPA-PC. At the industrially starting temperature of BPA polymerization, the rate constant would be very low for isosorbide-PC. The starting temperature of isosorbide transesterification should be shifted to above 190 °C to ensure an effective polymerization. An understanding of the temperature dependence of those systems are important to optimize the reaction conditions of both the homo-polymer and copolymer synthesis.

6.3.4 Impact of BPA concentration on rate kinetics

Along with the temperature dependence, the effect of BPA/isosorbide in copolymerization systems on the rate constant important to understand.

In this research, the overall average rate constant based on generation of phenol was used to evaluate polymer chain growth. The relative inclusion of BPA and isosorbide will be discussed in Section 6.4 in framework of a model developed to describe the chain growth.
Specifically, the rate constants for copolymers of isosorbide/BPA-PC of over full composition range determined at 190°C using phenol concentration as shown in Figure 6-6 and Table 6-4. The methods outlined in section 6.3.1 and Figure 6.4(a) were used to evaluate overall rate constant for reaction of hydroxyl end group with DPC end group in copolymers.

Figure 6- 6 Effect of monomer composition on the overall average rate constant for the BPA/isosorbide copolymerization reactions at 190°C
Table 6-4 Rate constant of BPA/isosorbide copolymerizations of different monomer compositions 190°C

<table>
<thead>
<tr>
<th>Isosorbide %</th>
<th>0</th>
<th>25</th>
<th>50</th>
<th>75</th>
<th>95</th>
<th>100</th>
</tr>
</thead>
<tbody>
<tr>
<td>BPA%</td>
<td>100</td>
<td>75</td>
<td>50</td>
<td>25</td>
<td>5</td>
<td>0</td>
</tr>
<tr>
<td>k (10^6 mol² min⁻² mL⁻²)</td>
<td>4.40±0.04</td>
<td>2.97±0.03</td>
<td>2.02±0.01</td>
<td>1.58±0.01</td>
<td>1.91±0.03</td>
<td>2.10±0.03</td>
</tr>
</tbody>
</table>

At 190°C, in the range of 0%-50% BPA, the rate constant initially decreased, then increased to value similar to 100% isosorbide rate constant. As the BPA concentration was larger than isosorbide, the rate constant increased almost linearly with the increasing BPA composition to the max value for pure BPA. The copolymer exhibited a minimum rate constant at 25% BPA-75% isosorbide.

In this study, it proved that when there is a big difference in the rate constant value, the percentage of the monomer with a higher rate constant plays a more important part effecting the rate constant value of the copolymer systems. When the composition of BPA exceed isosorbide, a significant increase in the rate constant value was observed. And in the range where the majority of the monomer is isosorbide, the k values are all relatively too low compared to BPA.

6.4 Equilibrium Study at 190°C

In industrial production, high vacuum is typically required in order to achieve high molecular weight BPA PC through melt phase polymerization. Because the transesterification of BPA and DPC is restricted by equilibrium, without removing the byproduct phenol, the reaction will reach equilibrium at low conversion.
The equilibrium behavior of isosorbide melt phase polymerization has not been reported in literature yet. An equilibrium study was performed to understand the equilibrium of pure isosorbide melt phase polymerization, the impact of monomer composition on the BPA/isosorbide copolymerization equilibrium, and the impact of temperature on the equilibrium.

6.4.1 Phenol conversion profile

The rate constant studies discussed in section 6.34 focused on the early stage of the polymerization reactions to avoid impact of equilibrium limitation. The percentage of DPC converted to phenol (P%), calculated using Equation (6-5) during full 100 min of reaction can be used to compare the equilibrium behavior of reactions. Phenol was chosen because it is the only byproduct of both the BPA-PC and isosorbide-PC reactions. The concentration percentage of phenol as a function of time for pure BPA-PC, isosorbide-PC and 50BPA/50isosorbide are given in Figure 6-7 to 6-9 for reaction temperatures from 165°C to 210°C.
Figure 6-7 Phenol conversion profile over time for transesterification of (▲)100% BPA, (♦)100% isosorbide, (■) and 50%BPA/50%isosorbide at 165°C.

Figure 6-8 Phenol conversion profile over time for transesterification of (▲)100% BPA, (♦)100% isosorbide, (■) and 50%BPA/50%isosorbide at 190°C.
The P% which is defined as the ratio of phenol to total phenolic end groups initially increased as a function of time up to approximately 50% conversion for the BPA-PC for all temperature studied. According to the equilibrium constant value reported in Kim’s work [13], the P% value was 51% and 53% at 180°C and 210°C, which was consistent with this research.

A batch reactor was used for this experiment where all the phenol generated was kept in the reactor. As the phenol accumulated, the reaction stopped moving forward and equilibrium was achieved. In industrial BPA-PC production, high vacuum and good mixing are used to ensure phenol removal to achieve high molecular weight polymer [53].

Figure 6- 9 Phenol conversion profile over time for transesterification of (▲)100% BPA, (♦)100% isosorbide, (■) and 50%BPA/50%isosorbide at 210°C
Because the rate constant of isosorbide-PC at 165°C is so low, a relatively small amount of phenol was generated and no equilibrium was observed within the 100 min measurement range. A similar result was seen for the 50% BPA/50 isosorbide copolymer at 165°C.

The melt phase transsterification of BPA-PC at 190°C exhibited large phenol generation rate and reached equilibrium in less than 20 min. The equilibrium can be still found at 50% conversion of phenol. While there was a significant increase in the phenol generation rate for isosorbide-PC, the conversion of DPC to phenol continued to climb to about 80% at 90 min with no evidence of equilibrium. The generation rate of the equal molar copolymer is slightly smaller than isosorbide-PC, similarly generation of phenol for the copolymer increased beyond the pure BPA-PC without achieving equilibrium.

The phenol generation of pure BPA-PC at 210°C is consistent with the outcomes of lower temperatures in Figure 6-7 and 6-8, with a more rapid phenol generation rate and equilibrium of 50% conversion. For the isosorbide-PC, equilibrium was not observed after P% reached about 86%. The phenol generation rate of equal molar copolymerization is between the two homo-polymerizations, and it appeared to reach equilibrium at 70%.

However, data were need after 40 min to support this conclusion.

In summary, the equilibrium restriction of BPA transesterification occurred at all temperatures and is consistent with what reported in the literature [13]. Interestingly, the equilibrium of isosorbide-PC was quite different from BPA. Specifically, the transesterification of isosorbide-PC did not exhibit equilibrium at conversion up to 100 minute at temperatures tested. At 210°C, the conversion of DPC to phenol was 86% without evidence of equilibrium. The 50%BPA/ 50% isosorbide copolymer did not reach
equilibrium at low temperature due to too slow kinetics, but approached equilibrium at about 70% conversion.

Based on the study of equilibrium study of isosorbide-PC. A synthesis experiment was carried out in a batch reactor with the phenol generated building up in the reactor. In previous work, where vacuum pump was applied to remove phenol during the reaction, the molecular weight of isosorbide-PC produced was too low to allow precipitation. A similar approach may be used in future studies to achieve good conversion of isosorbide-PC for prepolymers. This prepolymers could be used in traditional melt phase polymerization format.

6.4.2 Phenol conversion profile and BPA hydroxyl group profile and at 190°C

The equilibrium kinetics of isosorbide and BPA copolymerizations were studied at 190°C over full range of BPA/isosorbide copolymerization. The polymer chain was monitored using phenol generation (Figure 6-10) and reactive BPA hydroxyl group (Figure 6-11).
Equilibrium was observed in the 100% BPA at 50% and 75%BPA/25% isosorbide at 50%-60% in terms of phenol generation. For all the other copolymers, phenol was still being generated up to minutes in the batch reactor which is consistent with non-equilibrium conversions. Additionally, the higher the percent isosorbide in the reaction mixture, the higher final P% value was achieved. The 95%BPA/5% isosorbide curve showed a higher P% value at 90 minute than the 100% isosorbide, which may be due to
difference in k values. The overall reaction kinetics of equilibrium for the copolymerization was evaluated using the ratio of phenol to DPC conversion.

The relative rate of incorporation of BPA and isosorbide into the polymer backbone can be analyzed in terms of reaction of hydroxyl groups of BPA.

As defined earlier in Equation 6-3, the A\% is the ratio of unreacted hydroxyl groups of BPA to total hydroxyl groups for BPA using NMR analysis. Figure 6-11 provided a comparison of time dependence of unreacted BPA hydroxyl groups for homo-polymers and copolymers of BPA/isosorbide with DPC at 190°C. At 190°C the rate constant of BPA is higher than isosorbide, so that BPA would be incorporated into backbone at low reaction time.
Figure 6- 11 A% profile of of (■)100% BPA, (▲)75% BPA-25% isosorbide, (*50%BPA- isosorbide, (Δ)25% BPA-75%isosorbide, and (●) 5% BPA-95% isosorbide polymerization systems at 190°C

The A% of 100% BPA and 75%BPA/25% isosorbide curves initially decreased and become constant after equilibrium achieved, but for the systems with an isosorbide composition higher than 50%, the A% initially decreased, plaited for a time and increase at long time. And very low BPA concentration feed, a sharp increase in A% value was observed after 30 minutes.

The increase of A% value indicated that the transesterification reaction of BPA was moving in reverse due to production of phenol by isosorbide and DPC reaction (Figure 6-10). This indicates that BPA was depolymerizing from the polymer chain. The P% value
in Figure 6-10 of these systems was increasing over the entire measurement, which means the overall reaction was still moving forward with increasing polymer molecular weight.

These observations can be explained in terms of assumptions that the polymerization of isosorbide and BPA are two separate reactions, the BPA transesterification is equilibrium restricted, while isosorbide is not equilibrium limited up to 86% conversion of isosorbide. So that the transesterification of isosorbide keeps going on, leads to the accumulation of phenol, which causes the BPA transesterification moving to reverse and produce BPA hydroxyl end groups.

These results indicate that the BPA initially reacts with DPC to form oligomers with production of phenol. The buildup of phenol in systems leads to equilibrium for BPA-PC reaction. Since the isosorbide-PC reaction does not exhibit equilibrium at conversion up to 86%, thus isosorbide will continue to react with DPC and generate additional phenol. This would result in reverse reaction and depolymerization of BPA from backbone, which is consistent with the decrease in BPA hydroxyl groups for BPA/isosorbide copolymers followed by sharp increase after equilibrium is reached for BPA.

6.4.3 BPA equilibrium constant calculation

The equilibrium constant of BPA transesterification can be defined using expression reported by Gross et al. [62] in terms of concentration of end groups, phenol and carbonate linkage of PC.

\[ K_{eq} = \frac{[\text{carbonyl linkages}][\text{phenol}]}{[\text{hydroxyl groups}][\text{phenoxy groups}]} \]

This can be translated into
\[ K_{eq} = \frac{[1-A\%][P\%]}{[A\%][1-P\%]} \quad (6-8) \]

The \( K_{eq} \) values of BPA transesterification at different temperatures were calculated using the value of A\% and P\%, presented in section 6.2, when equilibrium was reached as shown in Table 6-5.

Table 6- 5 Equilibrium constant of BPA transesterification with DPC at different temperatures

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>165</th>
<th>190</th>
<th>210</th>
</tr>
</thead>
<tbody>
<tr>
<td>( K_{eq} )</td>
<td>1.33</td>
<td>1.3</td>
<td>1.26</td>
</tr>
</tbody>
</table>

The \( K_{eq} \) values reported in Gross’s work for these temperatures are 1.8, 1.6, and 1.5 [62]. The \( K_{eq} \) values are exhibit a small decrease as temperature increases, and this is consistent with a slightly exothermic reaction. Similar behaviors were also observed in the kinetics study of polyesters and polyamide step polymerizations[62].

6.5 BPA- isosorbide kintic model at 190°C

A model was developed to describle concentrations of species in reaction as a function of time for copolymers.

Therefore, assumptions were made in description the system.

I. In the copolymerization systems, at the early stage, the transesterification polymerization of BPA and isosorbide occur independently. The rate constant for pure component BPA-DPC and isosorbide-DPC were used to describe copolymerzation.
II. BPA transesterification is equilibrium restricted at 50% phenol conversion at 190°C with $K_{eq} = 1.31$.

III. The backward reaction of isosorbide transesterification was negligible at that temperature. This is based on observations that no equilibrium was reached at up to 86% phenol conversion for pure isosorbide-PC.

Based on these assumptions, the kinetics of the copolymerization can be expressed as

\[ \begin{align*} 
A + B & \rightleftharpoons C + P \\
I + B & \longrightarrow D + P 
\end{align*} \]

Where $A$ and $I$ are hydroxyl end groups provided by BPA and isosorbide separately, $B$ is phenolic end group of DPC, $C$ and $D$ are BPA-PC and isosorbide-PC repeat units, and $P$ is phenol. The hydroxyl groups of BPA or isosorbide included end group of monomer (2 groups) and growing chain group. The phenolic end groups include two for monomer and one for polymer chain end group. The change in concentrations of all the components change over time can be expressed in Equation (6-12) to (6-17) for batch reactor,

\[
\begin{align*}
 k_1' &= k_1 / K_{eq1} \\
 \frac{d[A]}{dt} &= - (k_1[A][B] - k_1'[C][P]) \\
 \frac{d[I]}{dt} &= - k_2 [I][B] \\
 \frac{d[B]}{dt} &= - (k_1[A][B] - k_1'[C][P] - k_2 [I][B]) \\
 \frac{d[C]}{dt} &= k_1[A][B] - k_1'[C][P] \\
 \frac{d[D]}{dt} &= k_2 [I][B] \\
 \frac{d[P]}{dt} &= k_1[A][B] - k_1'[C][P] + k_2 [I][B]
\end{align*}
\]

To compare with the experimental data, the results calculated using the model were reported in the form of BPA hydroxyl group conversion (A%), and phenol conversion
(P%)

where

$k_1$ is the effective rate constant of BPA transesterification polymerization forward reaction.

$k_1'$ is the effective rate constant of BPA transesterification polymerization reverse reaction, $k_1'$ can be calculated through Equation (6-11) by definition.

$k_2$ is the effective rate constant of isosorbide transesterification polymerization. The value of $k_1$ and $k_2$ determined from pure component reacted at 190°C in section 6.3.1 were used in this model.

After substitution $k_1=12$, $k_2=4.3$, and $k_1'=9.2$ into Equation (6-9) to (6-15), the concentration of each component as a function of time was calculated with Matlab.

In order to compare with the experimental data, the result were converted to the percentage of DPC converted to phenol, and percentage of unreacted BPA hydroxyl group (A%) by Equation (6-16) and (6-17). Using those two parameters, the behavior of BPA in the copolymerization process, and the overall copolymerization kinetics can be studied independently and compared to experimental results.

The overall polymerization kinetics is plotted in terms of P% in Figure 6-12 homo-polymerization and copolymerizations of BPA-isosorbide with DPC at 190°C. The point are experimental data and lines represent the model based on values rate constant determined for homo-polymerzaiton measurements as calculated in Matlab.
Figure 6-12 Experimental and simulated results of phenol percent change over time for different homo-polymerization and copolymerization systems at 190°C
The simulated result in Figure 6-12 and 6-13 showed a good agreement with the experimental data for all the polymerization systems. The agreement supports the viability of assumptions. There is some deviations between model and expectations in results for copolymer which may be due to impact of copolymerization rate kinetics. And the can be used in the homo-polymerizations and copolymerizations of isosorbide and BPA with different monomer compositions.
6.6 Copolymer composition prediction

A model to describe reaction kinetics of BPA-DPC and isosorbide-DPC was described in section 6-5. This model can be used to simulate copolymerization using the pure components kinetics data. For example, this model allows prediction of relative incorporation of BPA to isosorbide within the polymer backbone for different reaction conditions.

In Figure 6-14, the ratio of isosorbide to BPA in backbone over time are presented for copolymerization systems with a) 95% isosorbide-5%BPA, b) 75% isosorbide-25% BPA, c) 50% isosorbide-50% BPA, d) 25% isosorbide—75% BPA at 165°C, 190, and 210°C. Included in each figure is a line that represented the feed ratio of isosorbide/BPA.
a) 95% isosorbide- 5% BPA

Isosorbide/BPA = 95/5

- 210°C
- 190°C
- 165°C

b) 75% isosorbide- 25% BPA

Isosorbide/BPA = 75/25

- 210°C
- 190°C
- 165°C
Figure 6- 14 Ratio of isosorbide versus BPA changes over time for copolymerization system a) 95% isosorbide-5%BPA, b) 75% isosorbide-25% BPA, c) 50% isosorbide-50% BPA, d) 25% isosorbide—75% BPA at 165°C, 190, and 210°C
Table 6-6 The time when the polymerized monomer composition equals the feeding ratio at different temperature for different copolymerization systems

<table>
<thead>
<tr>
<th>Isosorbide%</th>
<th>t' at 190°C (min)</th>
<th>t' at 210°C (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>95</td>
<td>30</td>
<td>5</td>
</tr>
<tr>
<td>75</td>
<td>38</td>
<td>5</td>
</tr>
<tr>
<td>50</td>
<td>45</td>
<td>5</td>
</tr>
<tr>
<td>25</td>
<td>48</td>
<td>5</td>
</tr>
</tbody>
</table>

As shown in Figure 6-14 at 165°C, because the reactivity of isosorbide is very low relative to BPA, the isosorbide/BPA ratio in backbone is always below the feeding ratio within the 100 minutes measurement.

At both 190°C and 210°C, the monomer ratio in the copolymer increased rapidly with time. At 210°C, the monomer ratio in the copolymer composition reached the feeding ratio within 5 minutes, the difference between different feeding compositions was negligible. Initially, the polymer is primarily BPA.

And at 190°C, as can be read from Table 6-6, the t' value increased as the composition of isosorbide increased in the feeding ratio. Which means the more BPA used, the longer it took for the monomer ratio in copolymer to reach the feed ratio.

This information can be used to direct the design of copolymerization method. For example, reaction that are started at 165°C will have a high initial concentration of BPA in the polymer with some incorporation of isosorbide. At high temperatures, the polymer composite would be closed to that of feed and a random copolymer would form.
6.7 In-situ polymerization kinetics

The impact of adding of ALNW on reaction kinetics was determined for BPA-PC using method described in section 6.3.1. The effect of adding nanofiller on the reaction kinetics was studied at 190°C following similar procedure for the BPA-PC kinetics experiment. For this research, 5% of ALNW was added during the kinetics measurement experiment. Small amount of reactant mixture was sampled out at different times, and analyzed using NMR. The kinetics curve of the in-situ polymerization with 5% ALNW added to the melt determined using Equation (6-1) and (6-2) are present in Figure 6-15 and 6-16.

![Figure 6-15](image-url)

Figure 6-15 Kinetics curve of AL-BPA-PC in-situ polymerization calculated using BPA hydroxyl group concentration compared with the kinetics curve of BPA transesterification with DPC at 190°C
Figure 6-16 Kinetics curve of AL-BPA-PC in-situ polymerization calculated using phenol concentration compared with the kinetics curve of BPA transesterification with DPC at 190°C

The data points of the in-situ polymerization totally overlapped with result of pure BPA-PC points as shown in Figure 6-16. The linear fitting is the same, and the BPA hydroxyl group concentration kept constant after equilibrium was reached. In this figure, it can be concluded that using BPA hydroxyl group as the parameter, the in-situ polymerization exhibited the same reaction kinetics as the BPA transesterification, including rate constant and equilibrium behavior.

And in Figure 6-16, it was observed that the data points of AL-BPA-PC did not totally overlapped with the BPA-PC points, although the two sets of points were close and the
slope of their linear fitting is almost the same. It is possible that this difference was caused by experimental error, as the error of the rate constant at this temperature is 10%. Therefore, the presence of ANLW did not affect rate kinetics for BPA-PC even though there are reactive hydroxyl groups on ALNW surface.

6.8 Summary

In this Chapter, the kinetics of BPA and isosorbide transesterification with DPC was studied and both rate constant and equilibrium behavior were determined. The model used to determine rate constant for BPA transesterification was validated using concentration of hydroxyl end groups and phenol generated. Isosorbide homopolymerization and copolymerization of isosorbide was also studied based on these model.

The rate constants of pure isosorbide, pure BPA polymerization, and equal molar BPA isosorbide copolymerization were studied at 165°C, 190°C, and 210°C. Arrhenius plots were drawn, and activation energies were calculated. It was figured out that the activation of isosorbide transesterification is 1.8 times higher than that of BPA. The rate constant of isosorbide is very low at the industrial starting temperature of BPA polymerization, which is 165°C. As temperature raised up, the rate constant quickly increased, and was compatible with BPA at 210°C.

The understanding of the temperature dependence is important to optimize copolymerization method. Random copolymer and block copolymer can be designed to synthesize by adjusting the operation temperature.

The composition dependence studied the effect of monomer composition on the reaction
rate constants at 190°C. When the isosorbide composition was over 50%, the rate constant of the copolymerization systems was almost the same as the pure isosorbide. When the composition of BPA is over 50%, the rate constant increased almost linear as the BPA composition increased.

In industrial production, high vacuum is applied to remove phenol to synthesize high molecular weight BPA-PC, because the transesterification of BPA is highly equilibrium restricted. But in the equilibrium study of isosorbide, it proved that although isosorbide and BPA are structurally similar, the equilibrium behavior of isosorbide is quite different from BPA. At 190°C, equilibrium was not observed from both the pure isosorbide and isosorbide dominated copolymer synthesis systems. Only when the composition of BPA was over 50% in the copolymer, equilibrium restriction was able to be observed again. The equilibrium study showed that the backward reaction of isosorbide transesterification at 190°C was negligible. Based on these observations, a model was developed to simulate the copolymerization of isosorbide and BPA at 190°C. The good agreement between the simulated result and the experimental data proved the reliability of this model.
Chapter 7

Conclusions and Recommendation for Future Work

7.1 Conclusions

The most widely used BPA-PC production route, phosgene route is of sustainable concerns, because the usage of organic solvent and phosgene and the source of BPA is non-renewable. The overall practical goal of this research was to apply the principle of green chemistry and engineering to the production of PC with property similar to BPA-PC. Transesterification polymerization with DPC was chosen as the synthesis method. Because this process has greatly reduced the usage of organic solvent and phosgene than the traditional phosgene route.

Isosorbide, a commercially available starch based diol; BHMF, a small furanic diol that is available on lab scale; BPF a furanic based monomer that mimicked structure of BPA were used as biosourced monomers in very small quantities by Dr. Suchecks’ group in Chemistry and was not sufficient to pursue polymerization studies beyond very preliminary work. The BHMF was not thermally stable at reaction conditions, it would degrade at room temperature over a few days. Therefore, this study focused on isosorbide-PC and copolymers with BPA-PC.

AL-PC nanocomposites were synthesized via in-situ polymerization with BPA-PC and
isisorbide-PC to improve mechanical and thermal properties of the PC produced. Several conclusions can be made through these studies.

I. Nanocomposites

1. AL-BPA-PC nanocomposites were successfully synthesized through melt phase in-situ polymerization. After isolating the nanocomposites into bulk PC and functionalized ALNW using Soxhlet extraction. The presence of covalent bond between ALNW and polymer matrix was proved by FTIR and TGA analysis.

2. The molecular weight of AL-BPA-PC produced through in-situ polymerization can be calculated using NMR end group analysis. Solid state polymerization at a gradually increased temperature from 200°C to 240°C was proved to effectively upgrade the molecular weight.

3. Improved heat resistance was observed after solid state polymerization for both BPA-PC and AL-BPA-PC nanocomposites. AL-BPA-PC nanocomposites exhibits higher maxim derivative weigh loss temperature than the BPA-PC using TGA analysis.

4. Enhanced mechanical properties were observed from AL-BPA-PC with loadings from 0.5%-2% by weight. The tensile strength and Young’s modulus did to continuously increase as the ALNW loading increase, which was observed in the previous work done by our group in the solution based in-situ polymerization. It is due to the insufficient mixing during the melt phase polymerization.

II. Isosorbide based polycarbonate and nanocomposites
1. Isosorbide-PC and isosorbide/BPA-PC copolymers with different monomer compositions were synthesized using melt phase polymerization. Isosorbide-BPA-PC copolymer with an isosorbide ratio of 95/5 was observed to have the highest molecular weight. The glass transition temperature of this copolymer is 155°C, which is 8°C higher than the commercial BPA-PC.

2. AL-isosorbide-BPA-PC nanocomposites was synthesized through in-situ polymerization. The covalent bond between the copolymer and the functionalized ALNW was proved by FTIR analysis similar as AL-BPA-PC nanocomposites. The possibility of synthesizing isosorbide based polymer through melt phase in-situ polymerization was proved.

III. BPA and isosorbide transesterification kinetics study

1. Reaction kinetics of the transesterification polymerization was studied. BPA hydroxyl group concentration and phenol concentration at different times can both be used to calculate the reaction rate constant of BPA transesterification with DPC. The reliability of the chosen model was proved by the agreement between two results calculated using two methods.

2. Rate constant of BPA transesterification, isosorbide transesterification, and equal molar BPA and isosorbide copolymerization were studied at different temperatures. The temperature dependence of the rate constant revealed that the activation energy of isosorbide transesterification was 1.8 times higher than that of BPA. The big difference between the rate constant of those two monomers at different temperatures can be used to design synthesis method to obtain random sequence or block copolymer by adjusting the reaction temperature.
3. The equilibrium study at 190°C showed that only BPA transesterification was limited by equilibrium restriction. The backward reaction of isosorbide transesterification was negligible within the measurement range. This can be used in the isosorbide-PC synthesis. High vacuum is not necessary to facilitate the polymerization moving forward.

4. A copolymerization model was established, based on the equilibrium behavior of isosorbide. Components concentration change over time of copolymerization systems with 100% BPA, 75% BPA-25% isosorbide, 50%BPA- isosorbide, 25% BPA-75%isosorbide, and 5% BPA-95% isosorbide were studied. The agreement between the results simulated through Matlab and the data acquired through experiments proved the reliability of the model. The assumptions made to build up the model were also proved.

5. The adding of ALNW during the transesterification of AL-BPA-PC nanocomposites in-situ polymerization process had no significant effect on the reaction kinetics from both rate constant and equilibrium. Hydroxyl groups on ALNW surface could participate in reaction, but were not present in sufficient concentration to impact the kinetics in range of initial rates.

7.2 Recommended Future Work

While some success were made in this research, there are some limitations need to be discussed to achieve further improvement.

1. The melt phase in-situ polymerization was proved to be valid to synthesize AL-PC nanocomposites. Further improvement of the equipment is required to
obtain better mixing, better temperature and atmosphere control of the reactor, in order to achieve high PC with higher molecular weight. At the same time, with better mixing, the functionalization of ALNW may be more sufficient. A significant improvement of mechanical properties is expected to be achieved.

2. Isosorbide-PC with high enough molecular weight could not be achieved at beginning, the copolymer of 95% isosorbide- 5% BPA successfully synthesized at high enough molecular weight to cast into solid films. The kinetics studies were aimed to explain the behavior of the copolymer. But only 190°C was thoroughly studied, and the information obtained was not sufficient enough to answer the question. Similar kinetics study should be done at higher temperatures to reveal the reason for the high molecular weight.

3. In-situ polymerizations of PC with other nanofiller are also recommended, such as carbon nanofiber, or carbon nanotube. To investigate if better electronic properties can be achieved through the in-situ polymerization.

4. The study of the reaction kinetics provided a theoretical basis about how to optimize the reaction procedures of isosorbide involved transesterification polymerization. In the future, more synthesis research can be done by applying the conclusions got from the kinetics study.
References


7. **Kim, W.B., U.A. Joshi, and J.S. Lee**, Making polycarbonates without employing phosgene: An overview on catalytic chemistry of intermediate and precursor


28. **Gillet, J.P., J. Gillet, and J. Gillett**, New isosorbide compounds, useful as polar head in surfactant, in monomer polymerization by condensation, preferably in the
manufacture of polyamide, or as crosslinking agent, and as synthetic intermediate.

U.S. Patent 6884842 B2, 2005

29. Ren, H., et al., Polyamide containing isosorbide unit and process for preparing the polyamide comprising reaction of diamine monomer with dichloride. Univ Qinghua (Uyqi-C).


37. **Yuji Terado, F., Masaru Wada**, Polycarbonateester copolymer; heat resistance while having adequate mechanical properties; optical disc substrate, sheet and container made from the copolymer. 2008.


44. **Jansen, B.J.P., et al.**, Renewable copolymers with aliphatic diacid or diol; high molecular weight and heat resistance while having a sufficiently low glass transition temperature to allow polymerization and processing without phase separation and degraded mechanical properties; thermoplastics. U.S. Patent 7666972 B2, 2010


Appendix A

Matlab Code of the Kinetics Model

function dc=WeiKineticsa(w,c);

% PFR
% c1 is BPA, c2 is Isosorbide, c3 is DPC, c4 is BPA-PC, c5 is Phenol and c6 is Isosorbide PC

dc=zeros(6,1);

vo=10.0;% vo in dm3/min

k1=1; Keq1=1.3; k2=1; kprime=k1/Keq1;

vo=10;

rate1=k1*c(1)*c(3)-kprime*c(4)*c(5);

rate2=k2*c(3)*c(2);

dc(1)=(-rate1)/vo; % Change in concentration of BPA

dc(2)=(-rate2)/vo; % Change in concentration of ISOsorbide

dc(3)=(-rate1-rate2)/vo; % Change in concentration of DPC

dc(4)=(rate1)/vo; % Change in concentration of BPA-PC

dc(5)=(rate1+rate2)/vo; % Change in concentration of Phenol

dc(6)=(rate2)/vo; % Change in concentration of IsosorbidePC
\[ [w,c] = \text{ode45}(\text{'WeiKinetics'},[0 50],[1.5 0.5 2 0 0 0]); \]

\text{vo}=10.0; \% \text{vo in dm}^3/\text{min}

\text{figure;} \text{plot}(w,c(:,1)/1.5,'--',w,c(:,2)/0.5,'.',w,c(:,3)/2)

\text{xlabel('w')}

\text{ylabel('Normalized moles Reactants 75\% BPA/25\% Isosorbide');}

\text{h=legend('BPA','Isosorbide','DPC',1);}

\text{figure;} \text{plot}(w,c(:,4),'-',w,c(:,6),'.',w,c(:,5))

\text{xlabel('w')}

\text{ylabel('Moles product 75\% BPA/25\% Isosorbide');}

\text{h=legend('BPA-PC','Isosorbide-PC','Phenol',4)}

\text{figure;} \text{plot}(w,c(:,1),'-',w,c(:,4))

\text{xlabel('w')}

\text{ylabel('Moles product');}

\text{h=legend('BPA','BPA-PC',4);}