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Chemistry of Benzocyclobutenone Polymers

by

Li Kuang, M. Sc. (Sichuan University)

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

Doctor of Philosophy

Department of Chemistry

Carleton University

Ottawa, Ontario, Canada

July 2001

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the Faculty of Graduate Studies and Research
acceptance of the thesis,

Chemistry of Benzocyclobutenone Polymers

Submitted by
Li Kuang, B.S., M.Sc.

in partial fulfilment of the requirements
for the degree of Doctor of Philosophy

Chair, Department of Chemistry

Thesis Supervisor

External Examiner

Carleton University
To My Parents
Abstract

The main objective of this thesis is to investigate the chemistry of the benzocyclobutenone-containing polymers. This requires the studies of the thermal and photochemical reactions of benzocyclobutenone (BCBO), in particular its cycloaddition and nucleophilic addition reactions, routes to incorporation of BCBO into a variety of polymers and applications in the polymer curing systems.

The gas-phase pyrolysis process is better for the large-scale preparation of BCBO than the multi-step solution process. The thermal and photochemical reactions of BCBO with alcohols proceed in a similar mechanism with the first-order kinetic, involving the formation of a reactive vinyl ketene as a rate-determining step (Chapter II).

Both addition and condensation polymers can be functionalized with the BCBO group, by either free radical polymerization with a vinyl BCBO monomer or post polymerization with aminobenzocyclobutenone (Chapter III). The introduction of BCBO into polymers allows further manipulation of the polymer structure via grafting, branching, and crosslinking.

A new approach to the controlled incorporation of [60]fullerene into polystyrene or polyethylene has been demonstrated using BCBO polymers in a thermal cycloaddition reaction with [60]fullerene. Modification of polymers in bulk and on the surface have been demonstrated using the photochemistry of BCBO and various alcohols. Polymethacrylates and polyimides that contain both the BCBO and hydroxyl groups are shown to be self photocurable in solution and in the solid state without a catalyst or initiator, which can be used for direct photopatterning of the substrate with a 3 μm line resolution.
Acknowledgments

This thesis would not have been completed or even started without the help and support of many people. I first want to express my sincere gratitude to my supervisor, Prof. Wayne Z. Y. Wang, for his enthusiasm, endless encouragement and superb guidance throughout all aspects of my Ph.D. program. I am also grateful to Dr. Jane Gao, for her invaluable help and understanding.

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In particular, I thank my husband, Changsong Liu, for his love, encouragement and support throughout all the years. Last but not least, I thank my parents for encouraging me to pursue my own goal in my life. I dedicated my thesis to them.
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Symbols and Abbreviation

\( \lambda \)  
Wavelength

\( \delta \)  
Chemical shift (ppm)

\( \lambda_{\text{max}} \)  
Wavelength at maximum absorption

[\( \eta \)]  
Inherent viscosity

AIBN  
2, 2'-Azobisisobutyronitrile

An  
Acrylnitrile

ATR  
Attenuated reflectance adaptation

BAC-M  
2,6-bis(4'-azidobenzylidene)-4-methylcyclohexanone

BCB  
Benzocyclobutene

BCBO  
Benzocyclobutenone

BMA  
n-Butyl methacrylate

C_{60}  
[60]Fullerene

d  
Doublet

dd  
Doublet of doublet

DMF  
N, N-Dimethylformamide

DMSO  
Dimethyl sulfoxide

DNQ  
Diazonaptoquinone

DSC  
Differential scanning calorimetry

EDC  
1-(3-(Dimethylamino)propyl)-3-ethylcarbodiimide

GC  
Gas chromatography

GPC  
Gel permeation chromatography
<table>
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<tr>
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<tr>
<td>HEMA</td>
<td>2-Hydroxylethyl methacrylate</td>
</tr>
<tr>
<td>HOAt</td>
<td>1-Hydroxy-7-azabenzotriazole</td>
</tr>
<tr>
<td>HOMO</td>
<td>Highest occupied molecular orbital</td>
</tr>
<tr>
<td>HRMS</td>
<td>High resolution mass spectroscopy</td>
</tr>
<tr>
<td>IR</td>
<td>Infrared spectroscopy</td>
</tr>
<tr>
<td>J</td>
<td>Coupling constant</td>
</tr>
<tr>
<td>LUMO</td>
<td>Lowest unoccupied molecular orbital</td>
</tr>
<tr>
<td>m</td>
<td>Multiplet</td>
</tr>
<tr>
<td>MMA</td>
<td>Methyl methacrylate</td>
</tr>
<tr>
<td>$M_n$</td>
<td>Number-average molecular weight</td>
</tr>
<tr>
<td>mp</td>
<td>Melting point</td>
</tr>
<tr>
<td>MS</td>
<td>Low resolution mass spectroscopy</td>
</tr>
<tr>
<td>MW</td>
<td>Molecular weight</td>
</tr>
<tr>
<td>$M_w$</td>
<td>Weight-average molecular weight</td>
</tr>
<tr>
<td>NMR</td>
<td>Nuclear magnetic resonance</td>
</tr>
<tr>
<td>PDI</td>
<td>Polydispersity index ($M_w/M_n$)</td>
</tr>
<tr>
<td>PE</td>
<td>Polyethylene</td>
</tr>
<tr>
<td>q</td>
<td>Quintet</td>
</tr>
<tr>
<td>s</td>
<td>Singlet</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning electron micrographs</td>
</tr>
<tr>
<td>St</td>
<td>Styrene</td>
</tr>
<tr>
<td>t</td>
<td>Triplet</td>
</tr>
<tr>
<td>TCE</td>
<td>1, 1, 2, 2-tetrachloroethane</td>
</tr>
<tr>
<td>Symbol</td>
<td>Term</td>
</tr>
<tr>
<td>-------</td>
<td>-----------------------------------</td>
</tr>
<tr>
<td>$T_d$</td>
<td>Decomposition temperature</td>
</tr>
<tr>
<td>$T_g$</td>
<td>Glass transition temperature</td>
</tr>
<tr>
<td>TG</td>
<td>Thermogravimetry</td>
</tr>
<tr>
<td>THF</td>
<td>Tetrahydrofuran</td>
</tr>
<tr>
<td>$T_m$</td>
<td>Melting temperature</td>
</tr>
<tr>
<td>$T_{\text{max}}$</td>
<td>Temperature at maximal peak height</td>
</tr>
<tr>
<td>TMS</td>
<td>Tetramethyilsilane</td>
</tr>
<tr>
<td>$T_{\text{RO}}$</td>
<td>Ring-opening temperature</td>
</tr>
<tr>
<td>UV</td>
<td>Ultraviolet</td>
</tr>
<tr>
<td>Vis</td>
<td>Visible</td>
</tr>
<tr>
<td>XPS</td>
<td>X-ray photoelectron spectroscopy</td>
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A large majority of polymeric materials in the end-use state exist in the form of a crosslinked network. The main representatives of conventional crosslinked polymers include vulcanized rubbers, thermosetting resins, adhesives, coatings, polymeric sorbents, and gels. Polymer curing takes place during or after processing and involves many chemical reactions, such as chain extension, grafting, dehydration, and crosslinking. The cured polymers usually have a three-dimensional crosslinked network. A crosslinked network can be obtained from a linear polymer containing a functional group capable of reacting with itself, or from a functionalized polymer and a crosslinking agent. Crosslinked polymers can also be obtained from a monomer with an average functionality greater than two. Distinct features of crosslinked polymers in comparison with non-crosslinked polymers are often presented by their improved dimensional, thermal, physical and chemical stabilities.

The need for polymers with high thermal stability and good mechanical properties at high temperatures has greatly increased in order to meet the demands of the aerospace and electronics industries. Polymers that can meet stringent requirements for high-temperature use are aromatic rigid-rod polymers. But most of them have poor processability or infusibility due to high glass transition (T_g) and melting temperatures (T_m). Introduction of a flexible linkage such as the ether and methylene moieties, or a pendant group improves the processability of these polymers. However, the glass transition temperature is also depressed by the presence of flexible groups, and hence lowers its use temperature. The decomposition temperature is also lowered by the
presence of aliphatic groups. The use of curing technology allows for the preparation and processing of insoluble polymers with desirable thermal and mechanical properties. Introduction of a crosslinkable group to the end or side chain of an oligomer has been widely used to achieve curing, due to the higher flow property of an oligomer compared to that of a high molecular weight polymer.¹

The polymer curing system must meet several basic requirements. First, the curing agents or crosslinkable groups should remain inactive during polymerization, but would react under different conditions (i.e. higher temperature or irradiation). The curing reaction should also take place in the solid state at required temperatures, but below its decomposition temperature. Finally, the curing reaction should be specific and proceeds rapidly.

I.1. Current Curing Systems

As previously mentioned, the curing reaction occurs by action of heat and light or both. The current curing systems can be classified into two major categories, one that is initiated thermally and the other that is initiated by light.

I.1.1. Thermal Curing Systems

I.1.1.a. Curing Systems With Volatile By-Products

Some commercial products are available typically as crosslinkable or curable polymers such as paints and coatings, which are cured in applications through extensive condensation reactions. During the cure, a small molecule is evolved. A typical example is one-component polyurethane coating, which consists of a diisocyanate masked with
phenol or oxime and a polyol. During thermal cure, the reactive diisocyanate is regenerated, along with a volatile phenol or oxime (Scheme I.1).

\[
\begin{align*}
\text{phenol} & \quad \Delta \\
\text{Crosslinked Polyurethane} & \\
\end{align*}
\]

**Scheme I.1.** One-component heat-curing polyurethane using a masked diisocyanate.

A triazene group has been used to thermally cure polyimides\(^2\) and poly(aryl ethers)s.\(^3\) A bis-triazene crosslinker thermally decomposes to generate an aryl diradical and a reactive aminyl radical, along with gaseous nitrogen. The aryl radical and aminyl radical further react with a polymer, leading to a crosslinked polymer with evolution of dimethylamine as a by-product (Scheme I.2).

\[
\begin{align*}
\text{Polymer} & \quad \Delta \\
\text{Crosslinking system} & \\
\end{align*}
\]

**Scheme I.2.** Crosslinking of a polymer using a bis(triazene).
I.1.1.b. Curing System Without Volatile By-Products

A curing system that does not generate any volatile by-products is preferred in industrial applications, as it is potentially a green-chemistry process and affords a void-free product. Several of such curing systems have been developed, based on the carbon-carbon bond coupling reaction. For example, the acetylene group has been used as an end group to crosslink polyimides.\(^4\) It has not however been determined unambiguously whether the curing reaction proceeds by cyclotrimerization\(^5\) or polymerization\(^6\) of the acetylene group. (Scheme I.3).

\[
R\equiv H \xrightarrow{\Delta} \begin{array}{c}
\begin{array}{c}
R \\
R
\end{array}
\end{array} + \begin{array}{c}
\begin{array}{c}
R \\
R
\end{array}
\end{array}
\]

**Scheme I.3.** Proposed curing reaction of the acetylene end group in polymer.

Another crosslinking system is based on paracyclophephane. Paracyclophephane has been used in thermal curing of poly(aryl ether)s\(^7\) and polyquinolines.\(^8\) Upon heating, the paracyclophephane ring opens to form a diradical intermediate, which then dimerizes and/or polymerizes (Scheme I.4).\(^9\)

**Scheme I.4.** Thermal reactions of paracyclophephane.
Thermal activation of benzocyclobutene (BCB) generates a highly reactive diene (o-quinodimethane), which can enter into a wide variety of reactions such as dimerization, oligomerization, and Diels-Alder cycloaddition (Scheme I.5). This latent diene group has been introduced as an end group\textsuperscript{10} or a pendant group\textsuperscript{11} to a wide variety of polymers such as polyimides,\textsuperscript{12} polyamide,\textsuperscript{13} poly (arylene ether)\textsuperscript{s}\textsuperscript{14} and polystyrene.\textsuperscript{15}

\begin{center}
\begin{tikzpicture}
\node at (0,0) {\Huge $\Delta$}
\node at (-2,0) {\Huge苯环}
\node at (3,0) {\Huge \textbf{Dimer}}
\node at (1.5,-1.5) {\Huge \textbf{Oligomer}}
\node at (2.5,-3) {\Huge \textbf{Diels-Alder product}}
\end{tikzpicture}
\end{center}

\textbf{Scheme I.5.} Thermal reactions of benzocyclobutene.

Biphenylene has been used for crosslinking the polyquinolines.\textsuperscript{16} However, the degree of crosslinking for the biphenylene end-capped polymer was not always high enough to affect the polymer properties,\textsuperscript{17} due to the fact that dimerization of the biphenylene radical is dominant which leads only to chain extension. Better results were obtained when a mixture of an acetylene compound and a biphenylene-terminated polymer was employed together in thermal cure via the formation of the phenanthrene group (Scheme I.6).\textsuperscript{18}
Scheme 1.6. Thermal reactions of biphenylene.

Epoxides react with a wide variety of functional groups (i.e. amine, alcohol, carboxylic acid or anhydride and with itself). Its reaction with a primary amine is used to produce a crosslinked network. The epoxide is usually introduced in the polymer at the chain ends and cured with an amine or a diamine.

I.1.2. Photocuring Systems

I.1.2.a. Photoinitiated Radical Polymerization

A radical polymerization can be initiated using a photoinitiator or photosensitizer, which absorbs the light and generates a radical that initiates the chain reaction. Acrylates are known to be polymerizable among many reactive monomers via a photoinitiated free-radical mechanism (Scheme I.7). If a multifunctional acrylate is used in the reaction, a crosslinked polyacrylate will be formed. Thus, the simplicity of radical polymerization and availability of a wide range of acrylate monomers account for the great commercial success of acrylate-based UV-curable resins. However, a few drawbacks exist in this
system, such as a relatively short self-life time of the monomers and a possible quenching of radical chain propagation with oxygen in the air.

\[
\text{In} \xrightarrow{\text{hv}} \text{In}^* \\
\text{In}^* + \text{COOR} \rightarrow \text{In}^\cdots \text{COOR} \rightarrow \text{In}^\cdots \text{COOR}
\]

Scheme I.7. Photoinitiated radical polymerization of acrylate monomers.

I.1.2.b. Photoinitiated Cationic Polymerization

Protonic acids are readily generated by photolysis ofonium salts in the presence of a hydrogen donor molecule. The most efficient photoinitiators contain diaryliodonium or triarylsulphonium cations and fluorinated anions, such as BF$_4^-$, PF$_6^-$, AsF$_6^-$ or SbF$_6^-$.

The two distinct features of photoinitiated cationic polymerization are its lack of sensitivity toward atmospheric oxygen and its living character, due to the fact that the propagating polymer cations are not reacting among themselves. In contrast to radical initiated polymerization, the chain reaction will continue to proceed effectively after UV exposure.$^{19,20}$

Photoinitiated cationic polymerization is used to cure multifunctional monomers that are inactive towards radical species, in particular epoxides and vinyl ethers. The ring-opening polymerization of epoxides proceeds efficiently in the presence of a photogenerated protonic acid, with oxonium ions as a reactive species, to ultimately produce a polyether (Scheme I.8). Vinyl ethers do not homopolymerize in the presence
of free-radical initiators because of their electron-rich double bonds, but they do undergo a very fast cationic polymerization in the presence of protonic acids.

Scheme I.8. Photoinitiated cationic polymerization of epoxide.

Photoinitiated cationic polymerization has not experienced as fast a growth in UV-curing applications as free radical polymerization, mainly because of cure speed, product properties, and cost considerations. This situation may change in the future with appearance of new highly reactive epoxy monomers containing siloxane groups,\textsuperscript{21} which are shown to polymerize surprisingly fast upon UV irradiation in the presence of an onium salt.

I.1.2.c. Photocycloaddition Reaction

Poly(vinyl cinnamate) is one of the best known examples of photocurable polymers that undergoes a \([2+2]\) cycloaddition reaction.\textsuperscript{22} Crosslinking involves activation of the cinnamate ester chromophore by UV light, followed by reaction of the activated chromophore with a second cinnamate unit which is in the ground state.\textsuperscript{23} This results in the formation of a substituted truxillic ester (Scheme I.9).

I.1.2.d. Photoinitiated Nitrene Reaction

It is known that photolysis of an azide generates a nitrene species and a molecular nitrogen. A reactive nitrene intermediate can undergo a variety of reactions, including the nitrene-nitrene coupling to form an azo compound, insertion into a carbon-hydrogen bond to form a secondary amine, abstraction of the hydrogen from a hydrocarbon and insertion into a carbon-carbon double bond to form a cyclic amine. A well-known azide crosslinker is 2,6-bis(4'-azidobenzylidene)-4-methylcyclohexanone or BAC-M (Figure I.1). It has been widely used in the formulations of photoresist materials for photolithography,\textsuperscript{24} such as Kodak’s KTFR negative photoresist containing a cyclized cis-1, 4-polyisoprene and BAC-M (Figure I.1).
Figure 1.1. Cyclized cis-1, 4-polyisoprene and an azide crosslinker BAC-M.

Benzocyclobutenes (BCB) are a relatively new class of thermally crosslinkable polymers possessing desirable characteristics for use in the microelectronics and aerospace industries. In addition to thermal cure, benzocyclobutenes are also made into photocurable materials by Dow Chemical Company. A BCB monomer, 1,3-bis(2-bicyclo[4,2,0]octa-1,3,5-trien-3-yethenyl)-1,1,3,3-tetramethyl disiloxane, and a photocrosslinking agent, BAC-M, are typically formulated into a curable system. Upon irradiation at 310-340 nm, the azide decomposes to yield a reactive nitrene which further reacts with BCB. The primary event is the insertion of the nitrene into the carbon-carbon double bonds of BCB, leading to the formation of polymer networks (Scheme I.10).

Scheme I.10. Photochemistry of azide compounds.
I.1.2.e. Photoinitiated Carbene Reaction

A diazo compound, such as diazonaphthaquinone (DNQ), decomposes upon irradiation to yield a reactive carbene which undergoes a Wolff rearrangement reaction to form a ketene.\textsuperscript{28} The reactive ketene intermediate can then react with a nucleophile like alcohol and amine. A positive photoresist composed of DNQ and a Novolak phenolic resin for semiconductor fabrication is developed, based on the reaction of ketene and phenol (Scheme I.11).\textsuperscript{29,30} The resultant product has a quite different solubility than the starting phenolic polymer, which enables the wet etching and the pattern formation on a substrate. Conceivably, when a bis-DNQ compound is used, a crosslinked phenolic system will be formed.

Scheme I.11. The chemistry of the DNQ-Novolak photoresist.

I.2. Chemistry of Ketenes

As discussed above, the BCB and DNQ compounds are currently being used in several commercial curable polymer systems. The versatility of these compounds arise from the rich chemistry of diene (from BCB) and ketene (from DNQ). In fact, ketenes have been extensively studied and mainly utilized in the synthesis natural products. In order to fully appreciate the value of the ketene chemistry and further explore the
potential of ketenes in polymer systems, it is necessary to briefly review the ketenes and their chemistry.

Ketene is a linear molecule. The carbonyl (C=O) bond in ketene (C=C=O) is 1.16 Å in length, which is shorter than that of C=O (1.22 Å) in aldehyde and ketone. The shorter C=O bond in ketene implies an increase of the “triple bond” character. This increase in triple bond character arises from the relative importance of the resonance structure A over the two others (B and C) (Scheme I.12).

\[
\begin{array}{cccc}
\text{C=C=O} & \leftrightarrow & \text{C}^-\text{=O}^+ & \leftrightarrow \\
\text{C}_\beta \text{C}_\alpha & \text{A} & \text{B} & \text{C}
\end{array}
\]

\textbf{Scheme I.12. Resonance structure of ketene.}

The reactivity of ketene can be rationalized from the HOMO and LUMO geometry. The LUMO has been determined to be in the ketene plane with a higher coefficient on C_α whereas the HOMO is perpendicular to the ketene plane with a higher coefficient on C_β (Figure I.2). This implies that nucleophilic attack will occur at C_α and electrophilic attack at C_β of the ketene.

\textbf{Figure I.2. Molecular orbitals of ketene.}
I.2.1. Preparation of Ketenes

Ketenes can be prepared in numerous ways as shown in Scheme I.13. Most ketenes cannot be isolated due to their high reactivity. Hence, the formation of ketene is usually demonstrated via a trapping experiment and by isolating the products from its reactions with alcohol and cyclopentene.\(^\text{33-57}\)

The dehalogenation of 2-haloacyl halides in the presence of activated zinc is the oldest\(^\text{34}\) and the most widely used method to generate ketenes.\(^\text{35}\) The first ketene, diphenyl ketene, was prepared by Hermann Staudinger using dehalogenation of \(\alpha\)-bromodiphenylacetil bromide.\(^\text{34}\) This method gives excellent yields for stabilized ketenes. Metal anions such as \(\text{Mn(CO)}_5^-\) and \(\text{Cr(CO)}_4\text{NO}^-\) have also been shown to be effective in dehalogenation.\(^\text{36}\)

Dehydrohalogenation of acyl halides involved the elimination of hydrogen halide using a tertiary amine.\(^\text{37}\) The initial step of the reaction is the formation of an acylammonium salt.\(^\text{38}\) However, the use of tertiary amine may lead to other products.\(^\text{39}\) Monoalkylketenes cannot be prepared by this method since they dimerize in the presence of triethylamine hydrochloride. The dehydrochlorination of acyl chloride is also effected with a metal catalyst.\(^\text{40}\)

The preparative value of the Wolff rearrangement reaction arises from the reactivity and ready accessibility of \(\alpha\)-diazocarbonyl. The rearrangement can be triggered thermally,\(^\text{41}\) photochemically\(^\text{42}\) or by metal catalysts.\(^\text{43}\) The Wolff rearrangement provides a very versatile method for the preparation of ketenes with a wide variety of structural types. However, side reactions such as C-H insertion by the
carbene intermediate\textsuperscript{44} or fragmentation of the ketene\textsuperscript{45} is more likely to occur in a thermal or catalyzed reaction than in a photochemical one.

Alkylketenes can be obtained by reaction of carboxylic acid over alkali metal-exchange zeolite.\textsuperscript{46} Direct dehydration of a carboxylic acid also leads to the formation of ketene.\textsuperscript{47} Alkylketenes\textsuperscript{48} and the parent ketene\textsuperscript{49} are also produced by pyrolysis of acid anhydride. Photochemical decomposition of cyclic ketones provides ketenes via a biradical.\textsuperscript{50} Most of the reactions are carried out in alcoholic solvents, and as a result the ketene is converted to the ester.\textsuperscript{51}

Ketenes can also be obtained by thermolysis of alkynyl ethers.\textsuperscript{52} The main drawback of this route is the availability and stability of the alkynyl ether under the reaction conditions.\textsuperscript{53}

Ketene is also produced by reverse [2+2] or [4+2] cycloaddition reaction. Thermal decomposition of cyclobutane-1,3-dione (ketene dimer) regenerates ketene. The photochemical decomposition also leads to ketene but lower yields are obtained due to side reactions.\textsuperscript{54} Cyclobutanone and cyclobutenone produce ketenes by thermolysis\textsuperscript{55} or photolysis.\textsuperscript{56} The cleavage is thought to proceed via a biradical, but alternative paths cannot be excluded.\textsuperscript{57}
- Dehalogenation

\[
\begin{align*}
\text{Ph} & \quad \text{Ph} \\
\text{Br} & \quad \text{Br} \\
\text{O} & \quad \text{Zn} \\
\text{Ph} & \quad \text{Ph} \\
\text{C} & \quad \text{C} \quad \text{O} \\
\end{align*}
\]

- Dehydrohalogenation

\[
\begin{align*}
\text{R}_1 & \quad \text{R}_2 \\
\text{O} & \quad \text{NE}_3 \\
\text{R}_1 & \quad \text{R}_2 \\
\text{C} & \quad \text{C} \quad \text{O} \\
\end{align*}
\]

- Wolff rearrangement

\[
\begin{align*}
\text{Ph} & \quad \text{Me} \\
\text{O} & \quad \Delta \text{ or } \text{hv} \\
\text{Ph} & \quad \text{Me} \\
\text{C} & \quad \text{C} \quad \text{O} \\
\end{align*}
\]

- Dehydration of carboxylic acid

\[
\begin{align*}
\text{H}_3\text{C} & \quad \text{O} \\
\text{OH} & \quad \Delta \quad \text{-H}_2\text{O} \\
\text{H} & \quad \text{C} \quad \text{C} \quad \text{O} \\
\end{align*}
\]

- Decomposition of acetic anhydride

\[
\begin{align*}
\text{H}_3\text{C} & \quad \text{O} \quad \text{O} \quad \text{CH}_3 \\
\Delta & \quad \text{-acetic acid} \\
\text{H} & \quad \text{C} \quad \text{C} \quad \text{O} \\
\end{align*}
\]

- Decomposition of cyclic ketone

\[
\begin{align*}
\text{O} & \quad \text{hv} \\
\text{H}_3\text{C} & \quad \text{CH} \quad \text{C} \quad \text{O} \\
\end{align*}
\]

- Decomposition of alkynyl ether

\[
\begin{align*}
\text{H}_3\text{C} & \quad \text{O} \quad \text{O} \quad \text{CH}_2 \quad \text{CH}_2 \\
\text{H}_2\text{C} = \text{CH}_2 & \quad \text{-H}_2\text{C} = \text{CH}_2 \\
\text{H}_3\text{C} & \quad \text{O} \quad \text{CH} = \text{C} \quad \text{O} \\
\end{align*}
\]

- From cyclobutanone

\[
\begin{align*}
\text{O} & \quad \Delta \\
\text{H} & \quad \text{C} \quad \text{C} \quad \text{O} \\
\text{H} & \quad \text{H} \\
\text{H} & \quad \text{C} \quad \text{C} \quad \text{O} \\
\end{align*}
\]

\[\text{H}_2\text{C} = \text{CH}_2\]

Scheme 1.13. Routes to ketene formation.
1.2.2. Reactions of Ketenes

Ketenes are very reactive towards both unsaturated compounds and nucleophiles.\(^ {58}\) However, the [2+2] cycloaddition of ketene is by far the most synthetically useful reaction of ketenes. Additions of alcohol, amine or acid are not usually used in synthesis as the corresponding ester, amide or anhydride can be obtained by simpler methods.

1.23.2.a. Cycloaddition Reaction

Ketenes react with unsaturated compounds to produce the [2+2] cycloadduct. Ketenes react with carbon-carbon double\(^ {59}\) and triple\(^ {60}\) bond to from cyclobutanone and cyclobutenone respectively. Ketenes also react with carbonyl,\(^ {61,62}\) imine\(^ {35,63}\) and azo compound\(^ {64}\) to yield four-membered cyclic 2-oxetanones, 2-azetidinones and diazetidinones, respectively (Scheme I.14). The cyclobutanones formed by the reaction of a ketene with cyclopentadiene were found to be versatile intermediates\(^ {65}\) in the synthesis of tropones.\(^ {66}\) Ring contraction of α-halocyclobutanone produces cyclopropanes.\(^ {67}\) Decarbonylation of β-lactone yields alkenes.\(^ {68}\)

The [2+2] cycloaddition is the predominant cycloaddition reaction of ketenes. However, in few cases ketene is the dienophile in [4+2] cycloaddition in reactions with selected dienes or β-unsaturated ketones.\(^ {69}\) The [4+2] cycloaddition is a more common reaction for vinyl-\(^ {70}\) and oxo-ketene\(^ {71}\) (Scheme I.15). The [4+2] cycloaddition of acyl ketene is used in the syntheses of compounds with a herbicidal activity\(^ {51}\) and an HIV protease inhibitor.\(^ {72}\)

I.2.2.b. Nucleophilic Addition Reaction

Ketenes also react with nucleophiles such as hydride,\textsuperscript{73} water,\textsuperscript{74} alcohols,\textsuperscript{75} amines\textsuperscript{76} and amides\textsuperscript{77} to give the corresponding enol, ester, amide or imide (Scheme I.16). Intramolecular hydride attack occurs in 4-methylvinyl ketenes to form the corresponding aldehyde.\textsuperscript{78} The addition of alcohol was synthetically useful in the preparation of an unsaturated ester from vinyl ketene.\textsuperscript{79} Reaction with amines has been used in the synthesis of indolizidine and quinolizidine.\textsuperscript{80}

The nucleophilic attack also occurs at the $C_\alpha$ of the ketene. Electronic and steric effects of the ketene substituents were rationalized by an in-plane attack.\textsuperscript{33} When amine was used as a nucleophile, a zwitterionic intermediate has been observed by NMR spectroscopy.\textsuperscript{81}
- Hydride
\[
\begin{align*}
\text{Ph} & \quad \text{C} = \text{C} = \text{O} \\
& \quad \text{R} \\
\text{Ph} & \quad \text{O} \text{SiMe}_3 \\
\rightarrow & \quad 1. \text{LIAH}_4 \\
& \quad 2. \text{Me}_3\text{SiCl} \\
\rightarrow & \quad \text{Ph} \quad \text{R} \\
\text{C} & \quad \text{H} + \text{Ph} \\
& \quad \text{R} \\
& \quad \text{O} \text{SiMe}_3
\end{align*}
\]

- Water
\[
\begin{align*}
\text{Ph} & \quad \text{CO} \\
& \quad \text{H}_2\text{O} \\
\rightarrow & \quad \text{Ph} \quad \text{COOH} \\
\end{align*}
\]

- Alcohol
\[
\begin{align*}
\text{Ph} & \quad \text{C} = \text{C} = \text{O} \\
& \quad \text{MeO} \text{OH} \\
\rightarrow & \quad \text{Ph} \quad \text{MeO} \\
\end{align*}
\]

- Amine
\[
\begin{align*}
\text{Ph} & \quad \text{C} = \text{C} = \text{O} \\
& \quad \text{MeO} \\
& \quad \text{NH}_2 \\
\rightarrow & \quad \text{MeO} \quad \text{Ph} \quad \text{NH} \\
\end{align*}
\]

- Amide
\[
\begin{align*}
\text{Ph} & \quad \text{C} = \text{O} \\
\text{NHAr} & \quad \text{O} \\
\rightarrow & \quad \text{Ar} \quad \text{N} \quad \text{O}
\end{align*}
\]

Scheme I.16. Nucleophilic addition to ketenes.
1.2.2.c. Electrophilic Addition Reaction

Electrophilic addition on ketenes occurs with protons\textsuperscript{81} and metal alkoxides\textsuperscript{82} (Scheme I.178). Addition of carboxylic acid,\textsuperscript{83} phosphoric acid\textsuperscript{84} and sulfonic acid\textsuperscript{85} to ketenes produces mixed anhydrides.

- Protonation

\[
\begin{align*}
\text{H}_2\text{C}=&\text{C}=\text{O} \quad & \xrightarrow{H^+} & \quad \text{H}_3\text{C}=&\text{C}=\text{O} \\
\end{align*}
\]

- Reaction with metal alkoxides

\[
\begin{align*}
\text{H}_2\text{C}=&\text{C}=\text{O} \quad & \xrightarrow{\text{R}_n\text{MOR}} & \quad \text{R}_n\text{MH}_2\text{C}=&\text{C}=\text{O} \quad & \xrightarrow{\Theta} & \quad \text{R}_n\text{MCH}_2\text{CO}_2\text{R} \\
\end{align*}
\]

Scheme I.17. Electrophilic addition to ketenes.

1.2.2.d. Radical Addition Reaction

Radical additions to ketenes have been studied with the hydroxyl radical.\textsuperscript{86} The hydroxyl radical addition occurs on either carbon of the ketene and is followed by bond cleavage (Scheme I.18).

\[
\begin{align*}
\text{H}_2\text{C}=&\text{C}=\text{O} \quad & \xrightarrow{\text{HO}^+} & \quad \text{HOH}_2\text{C}=&\text{C}=\text{O} \quad & \xrightarrow{} & \quad \text{HOCH}_2 & + & \text{CO} \\
\text{H}_2\text{C}=&\text{C}=\text{O} \quad & \xrightarrow{\text{HO}^+} & \quad \text{H}_2\text{C}=&\text{CO}_2\text{H} \quad & \xrightarrow{} & \quad \text{CH}_3\text{CO}_2 \quad & \xrightarrow{} & \quad \text{CH}_3 \\
\end{align*}
\]

Scheme I.18. Reaction of hydroxyl radical with ketene.
I.3. Research Rationale and Objectives

Based on the survey results of the types of the curing polymer systems and curing reactions, it is clear that benzocyclobutene and ketene have their own distinct advantages and inherent disadvantages, as highlighted in Table I.1.

Table I.1. Comparison of BCB and ketene systems.

<table>
<thead>
<tr>
<th></th>
<th>Functionality</th>
<th>Major Reaction</th>
<th>Initiation</th>
</tr>
</thead>
<tbody>
<tr>
<td>BCB</td>
<td>latent diene</td>
<td>[4+2] cycloaddition</td>
<td>heat</td>
</tr>
<tr>
<td>Ketene</td>
<td>ketene</td>
<td>Cycloaddition nucleophilic addition</td>
<td>heat and light</td>
</tr>
</tbody>
</table>

In comparison, BCB is a stable molecule that can be incorporated into a variety of prepolymer but ketene offers more choices of reactions for one to develop new curing systems. However, ketene is too reactive to be present in a prepolymer. Thus, it is logic to propose that a molecule that has stability like BCB and reactivity like ketene, would be a novel curing agent. Such an agent would offer some unique features that neither BCB nor ketene does:

1. The presence of relatively stable, latent ketene and diene moieties,
2. Dual-mode (thermal and photo) initiation, and
3. Both cycloaddition and nucleophilic addition reactions available.

Considering the structural features of this proposed molecule, it actually resembles a class of compounds called cyclobutenone, which is known to undergo an electrocyclic ring-opening reaction to yield a reactive vinyl ketene (Scheme I.19).57
Scheme I. 19. A reactive vinyl ketene derived from cyclobuteneone.

Further comparing the structures of BCB and cyclobuteneone, one could realize a specific cyclobuteneone --- benzocyclobuteneone (BCBO) that upon activation by heat or light generates a reactive intermediate having the diene and ketene moieties (Scheme I.20).

Scheme I.20. Reactive diene and vinyl ketene derived from BCB and BCBO.

Although BCBO is structurally related to BCB, the chemistry of BCBO should be much richer than that of BCB as the former only contains a latent ketene moiety. It is therefore conceivable that the BCBO-containing polymers would also be more versatile in terms of the types of reactions they could have in comparison with the corresponding BCB-containing polymers. More specifically, the BCBO polymers should not only be able to undergo a thermally-initiated reaction as the BCB polymers, but also a photoinitiated reaction that the BCB polymers alone would not. Accordingly, it would be
important to study the chemistry of BCBO and would be beneficial to explore the applications of the BCBO chemistry in polymer curing systems.

The objectives of this thesis work are proposed as follows:

1. To study the scope and limitations of the chemistry of BCBO;
2. To incorporate BCBO into the polymer systems;
3. To investigate the curing chemistry of BCBO polymers;
4. To explore potential applications of BCBO polymers.

According to the research objectives, the following chapters describe the BCBO chemistry, incorporation of BCBO into polymers, and applications of the BCBO-polymers. Since the thermal reactions of BCBO (e.g., chain extension and grafting) had been studied in our lab, this thesis will focus on the photocuring chemistry of BCBO.
I.4. References


II. Synthesis of Benzocyclobutenone

II.1. Introduction

For a synthetic purpose, benzocyclobutenone may be considered a derivative of either benzocyclobutene or cyclobutenone. Benzocyclobutene (BCB) ring opens to give $\alpha$-quinodimethane which can be trapped with maleic anhydride. The ring-opening has been shown to be reversible. BCB has indeed been obtained from $\alpha$-quinodimethane generated by pyrolysis of 1,3-dihydroisothianaphthene-2,2-dioxide. The first synthesis of BCB was achieved via electrolyclization of $\alpha$-quinodimethane. Since then, BCB and several derivatives have been prepared by 1,4-elimination of hydrogen halide or dihalide, followed by ring closure (Scheme II.1).
Scheme II.1. Synthesis of benzocyclobutene by electrolyzation.

Cyclobutenones also undergo ring-opening upon thermolysis to yield a vinyl ketene. Early attempts to use the reverse reaction for the synthesis of cyclobutenone proved unsuccessful. Treatment of unsaturated acids with thionyl chloride in acetic acid did not yield the cyclobutenone. On heating of 2-chloro-3-phenyl-3-butenoic acid in acetic anhydride, a vinyl ketene was generated which did produce 2-chloro-3-phenyl cyclobutenone in 20% to 30% yield (Scheme II.2). The pyrolysis of 1-ethoxypentachloro-1,3-butadiene produced perchlorocyclobutenone in 85% yield. The Wolff rearrangement of diazoketone generated a vinyl ketene which underwent intramolecular cycloaddition to form a cyclobutenone with moderate to high yields.
Scheme II.2. Synthesis of cyclobutenones.

Cyclobutanone and cyclobutenone are more commonly prepared by [2+2] cycloaddition of a ketene with an alkene\(^{14}\) or an alkyne\(^{15}\) (Scheme II.3).

Scheme II.3. Reactions of ketene with alkenes and alkynes.
II.1.2. Synthesis of Benzocyclobutenone

The synthesis of benzocyclobutenone (BCBO) was first reported by Cava et al. in 1960 (Scheme II.4).\textsuperscript{16} Reaction of 1-bromobenzocyclobutene with silver trifluoroacetate produced benzocyclobutenyl trifluoroacetate. After hydrolysis, benzocyclobutenol was oxidized with chromic oxide in pyridine to yield BCBO. To date, many synthetic routes have been reported for the preparation of BCBO.\textsuperscript{16-23} The synthesis of BCBO can be achieved either by solution or gas phase chemistry. The solution chemistry involves the use of the benzyne intermediate, whereas in the gas phase BCBO is made by reverse electrocyclization of a vinyl ketene.

![Scheme II.4. Synthesis of benzocyclobutenone.](image)

In solution, the \textit{in-situ} generated benzyne reacts with an activated alkene (Scheme II.5) to form the cyclobutene. Benzyne can be generated either from anthranilic acid via diazonium salt,\textsuperscript{17} bromobenzene\textsuperscript{18} or \(o\)-iodobenzene triflate.\textsuperscript{19} The four-membered ring was formed by [2+2] cycloaddition of benzyne with either 1,1-dichloroethylene\textsuperscript{17} or 1,1,-dimethoxyethylene.\textsuperscript{18,19} Benzocyclobutenone was finally obtained by hydrolysis of 1,1-dichloro- or 1,1-dimethoxybenzocyclobutene.
Scheme II.5. Synthesis of benzocyclobutenone via benzyne.

Benzocyclobutenone has also been synthesized via electrocyclization of a vinyl ketene intermediate (Scheme II.6). o-Quinoid ketene was generated by pyrolysis of 1,2-indandione, 20 homophthalic anhydride, 21 bicyclo[2,2,1]hepta-2,5-diene-2,3-dicarboxylic anhydride 22 and o-toluoyl chloride. 23 Pyrolysis was accompanied by the evolution of carbon monoxide, carbon dioxide or HCl gas. The yield of benzocyclobutenone varied from 11 to 54%.

Both the solution and gas phase syntheses of benzocyclobutene were investigated in our lab. The following are the summaries of the two methods.

II.1.2.a. Solution Chemistry

Benzocyclobutene was prepared from 1,1-dichloroethylene and anthralinic acid. Benzyn was generated in situ by decomposition of the diazonium salt derived from anthralinic acid. Hydrolysis of 1,1-dichlorobenzocyclobutene with 3% sulfuric acid afforded BCBO with a 55% yield, similar to the reported one (60%).\(^\text{17}\) The moderate yield of this reaction was due to side reactions of the highly reactive benzyn. In the absence of a nucleophile, benzyn can dimerize to form biphenylene. Biphenylene is a common by-product in reactions proceeding via the benzyn intermediate. Thus, 1,1-dichloroethylene had to be used in excess in order to suppress the dimerization of benzyn. Furthermore, 1,1-dichloroethylene is volatile and slowly evaporates during the reaction, which may also account for the low yield.

II.1.2.b. Gas Phase Chemistry

Although BCBO can be prepared in over 100-gram scale in overall yield 55% yield by solution chemistry, this process is not environmentally friendly. The process involves the use of potentially explosive diazonium salt and large amounts of solvents (e.g., 1.5 liters of chlorinated solvent and 2 liters of diethyl ether for 80 g of BCBO) and as well produces a large amount of solid waste. On the other hand, the gas phase reaction is safer and cleaner as there is no solvent. Furthermore, the starting material, o-toluoyl
chloride, is commercially available or can be readily prepared from inexpensive o-toluic acid, which is derived from petrochemicals.

Thermal elimination of hydrochloric acid occurs readily with o-alkyl substituted acyl chloride. Schiess used this method of flash vacuum pyrolysis to prepare BCBO and some related derivatives. At 14 mmHg with a furnace temperature of 630 °C, BCBO was obtained only in 28% yield. The yield increased to 60-70% when a second methyl groups, in the ortho position to the methyl or acyl chloride in the starting material. The same procedure was used to prepare a pyridine analogue of BCBO. Pyrolysis of o-toluoyl chloride was also investigated in detail in our lab.

The pyrolytic apparatus was set up similar to a vacuum distillation system, in which the condenser was replaced by a quartz tube filled with quartz chips. The tube was placed in a tube furnace. The receiving flask was placed in a cold bath. The hydrochloric acid evolved was trapped in a column packed with potassium hydroxide pellets. It was found that the pyrolysis was sensitive to several parameters. The starting material should vaporize before entering the hot quartz tube. Then it should stay in the hot zone long enough to allow the formation of vinyl ketene intermediate. However, this reactive intermediate and the final product should be removed from the hot zone right away to prevent any further reaction or degradation. Consequently, the pressure and temperature in the system must be fine tuned in order to achieve a maximum yield. The reaction rate is controlled by the furnace temperature, while the system pressure governs the time that the reactant and the product travel through the hot zone. As a result, changes in pressure or temperature have dramatic effects on the reaction yield.
Some of pyrolysis parameters such as oven temperatures and system pressures were probed for a given pyrolysis setup in this laboratory. Thus, a series of experiments were carried out at higher temperatures in order to increase the reaction rate and at lower pressures to shorten the traveling time of the product in the hot zone. Overall, the yields of isolated BCBO were higher than the one reported by Schiess (28% yield, 630 °C at 14 mmHg). A gradual improvement in the yield was observed when the pressure was decreased from 14 to 5 mmHg and the temperature was set at 630 °C. At the pressure of 5 mmHg, an increase of the oven temperature from 630 °C to 780 °C had little effect on the yield. At 780 °C, a further decrease of the system pressure to 0.5 mmHg eventually reached an optimal point, giving the 80% yield of isolated BCBO. At a slightly higher temperature of 800 °C (at 0.5 mmHg), the yield went down noticeably, indicating a high sensitivity of this pyrolysis reaction.

The BCBO product was characterized by spectroscopic analysis. The IR spectrum showed the characteristic bands at 1782 and 1758 cm\(^{-1}\) (lit.\(^{17}\) 1775 and 1755 cm\(^{-1}\)). The \(^1\)H NMR spectrum exhibited one expected singlet at 3.97 ppm for the methylene moiety. The \(^{13}\)C NMR spectrum showed eight peaks corresponding to the eight chemically non-equivalent carbons of BCBO.

Some of the degradation products from BCBO have been identified, including benzocyclop propane,\(^{20}\) fulveneallene,\(^{20,21}\) and ethylInylcyclopentadiene\(^{20}\) (Scheme II.7).

\[
\begin{align*}
\text{BCBO} & \xrightarrow{\Delta} \text{BCB} + \text{C} = \text{C} \cdot \text{C} = \text{C} + \text{C} = \text{C} \\
\text{Scheme II.7. Thermal degradation products of benzocyclobutene}\n\end{align*}
\]
II.2. Reactions of Benzocyclobutenone

Benzocyclobutenone has been reported to undergo electrocyclic ring-opening upon thermolysis $^{27,28}$ or photolysis $^{27,29}$ to give an o-quinoid ketene (II-1) (Scheme II.8). This ketene, when generated at low temperature ($77K$), reverted back to benzocyclobutenone at elevated temperatures. $^{30}$ The loss of carbon monoxide was observed when the ketene II-1 was generated by pyrolysis or photolysis with a mercury lamp. Benzocyclopropene and its rearrangement product, fulveneallene, were formed. $^{27,31}$ Other vinyl ketenes have been reported to lose carbon monoxide when irradiated at 212 nm $^{32}$ and 308 nm. $^{33}$

Scheme II.8. Ring-opening of benzocyclobutenone.

The vinyl ketene II-1 undergoes [4+2] cycloaddition with unsaturated compounds to yield six-membered cyclic compounds (Scheme II.9). The cycloaddition proceeds with vinyl compounds such as dimethyl fumarate, $^{34}$ dimethyl acetylenedicarboxylate, $^{34}$ 1,4-naphthoquinone $^{34}$ and C$_{60}$, $^{35}$ and with carbonyl compounds such as chlorals $^{34a}$ and diethyl azodicarboxylate. $^{34a}$
Scheme II.9. Reaction of benzocyclobutenone with unsaturated substrates.

Cyclobutanone\textsuperscript{36} and cyclobutenone\textsuperscript{37} are labile to a hydroxide ion. Nucleophilic attack of the hydroxide at the carbonyl carbon, followed by bond cleavage produces the carboxylic acid. Similarly, treatment of BCBO with a hydroxide base (e.g., NaOH) produces two types of carboxylic acids via the intermediate II-2 (Scheme II.10).\textsuperscript{16}

\[
\text{Scheme II.10. Ring-opening of benzocyclobutenone with hydroxide ion.}
\]

II.2.1. Thermal Reaction of Benzocyclobutenone with Alcohols

The thermal reaction of BCBO with a stoichiometric amount of alcohols was previously investigated in this laboratory.\textsuperscript{38} In the presence of an alcohol, heating BCBO
at relatively low temperatures (170-200 °C) yielded the corresponding 2-methylbenzoates (II-3) in good to quantitative yields (Scheme II.11). Both aliphatic and aromatic diols of low or high molecular weights reacted with BCBO, giving the corresponding bis-benzoates (II-4) in quantitative yields. The reaction was run in a sealed tube placed in an oil bath. The reaction conditions and the results are summarized in Scheme II.11.

\[
\begin{array}{c}
\text{II-3} \\
\text{II-4}
\end{array}
\]

<table>
<thead>
<tr>
<th>R</th>
<th>% Yield</th>
<th>Conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>-CH₂(CH₂)₆CH₃</td>
<td>79.3%</td>
<td>(200 °C, 30h)</td>
</tr>
<tr>
<td>-CH(CH₃)₂CH₂CH₃</td>
<td>80.3%</td>
<td>(200 °C, 26h)</td>
</tr>
<tr>
<td>-C(CH₂CH₃)₃</td>
<td>no rxn</td>
<td>(170 °C, 19h)</td>
</tr>
<tr>
<td>-CH₂Ph</td>
<td>100%</td>
<td>(180 °C, 5h)</td>
</tr>
<tr>
<td>-PhC(CH₃)₂</td>
<td>100%</td>
<td>(200 °C, 2h)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>R</th>
<th>% Yield</th>
<th>Conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>-CH₂CH₂-</td>
<td>100%</td>
<td>(200 °C, 18h)</td>
</tr>
<tr>
<td>-PhC(CH₃)₂Ph⁻</td>
<td>100%</td>
<td>(200 °C, 2h)</td>
</tr>
<tr>
<td>-CH₃(CH₂OCH₂CH₂)ₓ⁻</td>
<td>100%</td>
<td>(190 °C, 18h)</td>
</tr>
</tbody>
</table>

Mw=600

**Scheme II.11.** Thermal reactions of benzocyclobutenone with alcohols.

II.2.2. Photochemical Reactions of Benzocyclobutenone with Alcohols

Although BCBO is known to undergo an electrocyclic ring-opening reaction upon photolysis\(^{27,29}\) to give vinyl ketene II-1 which should be able to react with an alcohol, the photochemical reaction of BCBO with alcohols has not been investigated in detail. A number of papers on the kinetic studies of the photochemical reactions of alcohols with cyclobutenones rather than benzocyclobutenone have been published.\(^{39-41}\) Therefore, it is necessary to investigate the kinetics of the photoreaction of BCBO with alcohols.
Thus, the photochemical reactions of BCBO with alcohols were examined (Scheme II.12). BCBO and alcohols were placed in a sealed UV cell (either in solution or neat) and subsequently irradiated with UV light at ambient temperatures. The spot UV light was used, at a wavelength range of 300–350 nm with an intensity of 1000 mW/cm². The reaction was monitored by gas chromatography (GC).

\[
\text{hv} \quad \overset{(k_1)}{\longrightarrow} \quad \text{II-1} \quad \overset{(k_2)}{\longrightarrow} \quad \text{II-3}
\]

\[R = \begin{array}{c}
-\text{CH}_2\text{(CH}_3\text{)}_6\text{CH}_3 \\
-\text{CH(CH}_3\text{)}_2\text{CH}_3 \\
-\text{CH}_2\text{Ph} \\
-\text{CH}_2\text{(CH}_2\text{)}_2\text{CH}_3
\end{array} \]

\[\text{a} \quad \text{b} \quad \text{c} \quad \text{d} \quad \text{f}\]

**Scheme II.12.** Photochemical reactions of benzocyclobutenone with alcohols.

Similar to the thermal reactions with alcohols, the yields of photochemical reactions were nearly quantitative (Table II.1). The reaction rates depend on the type of an alcohol and the reaction medium.

**Table II.1.** Photochemical reactions of BCBO with alcohols.\(^a\)

<table>
<thead>
<tr>
<th>Alcohol</th>
<th>Solvent</th>
<th>Time, min</th>
<th>GC Yield, %</th>
<th>(k_{\text{exp}} \times 10^{-4}, \text{s}^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-butanol</td>
<td>none</td>
<td>210</td>
<td>100</td>
<td>3.37</td>
</tr>
<tr>
<td>benzyl alcohol</td>
<td>none</td>
<td>210</td>
<td>99</td>
<td>3.82</td>
</tr>
<tr>
<td>2-octanol</td>
<td>none</td>
<td>150</td>
<td>98</td>
<td>4.65</td>
</tr>
<tr>
<td>1-octanol</td>
<td>none</td>
<td>150</td>
<td>100</td>
<td>5.53</td>
</tr>
<tr>
<td>1-octanol</td>
<td>DMF (^b)</td>
<td>90</td>
<td>100</td>
<td>5.57</td>
</tr>
<tr>
<td>1-octanol</td>
<td>ethyl ether (^b)</td>
<td>90</td>
<td>98</td>
<td>7.72</td>
</tr>
<tr>
<td>1-octanol</td>
<td>cyclohexane (^b)</td>
<td>70</td>
<td>99</td>
<td>12.25</td>
</tr>
</tbody>
</table>

\(^a\)At 22 °C using a stoichiometric amount of alcohol. \(^b\)Same to alcohol in volume.
**Reaction time:** It can be seen from Table II.1 that the photochemical reactions were much faster than the same thermal reactions (~ 20 hours). This implies that the vinyl ketene II-1 is formed preferably under the photochemical conditions than the thermal conditions.

**Solvent polarity:** As the photochemical reactions were carried out in neat and in solvents, the effect of the reaction medium on the reaction rate could be probed. It has been found that the polarity of the reaction medium affects the reaction rate or BCBO conversion (Figure II.1). In a non-polar solvent such as cyclohexane, the reaction proceeded very quickly. However, the reaction rate decreased as the solvent became more polar (in the order of ethyl ether to DMF). The same trend can also be seen when the reaction was performed even in neat, considering the alcohol as a reactant and a solvent as well. For example, the reaction rate increased with the decrease in polarity of the reactants going from n-butanol, benzyl alcohol, 2-octanol to 1-octanol. A small inverse dependence of the measured rate on the solvent polarity is agreement with a concerted electrocyclic ring opening of BCBO. Since the dipole moments of ketenes are reported to be smaller than those of analogously substituted ketones, the same relationship should be valid for cyclobutenones (e.g., BCBO) and vinyl ketenes (e.g., II-1).
Figure II.1. Effect of the solvent polarity on the rate of the photochemical reactions of BCBO with alcohols.

Reactant: BCBO can react with a variety of alcohols upon UV irradiation. There was not much difference between aliphatic and benzylic alcohols as can be seen in Figure II.2, although the former reacted a bit faster. Among the aliphatic alcohols used, primary alcohols reacted faster than the secondary ones (Figure II.3). No reaction was observed with a tertiary alcohol, indicating a steric effect of a bulky alcohol. The selectivity of alcohols in the reaction with ketenes has been studied by Schyja et al. A primary alcohol reacts faster than a secondary one and much faster than a tertiary one. This selectivity, rationalized in terms of steric hindrance, and was found to be valid in the presence or absence of base as a catalyst.
Figure II.2. Comparison of the photochemical reactions of BCBO with aliphatic and benzyl alcohols.

Figure II.3. Comparison of the photochemical reactions of BCBO with primary and secondary alcohols.
Kinetic studies: The values of \( \ln[\text{BCBO}] \) versus reaction time for the reactions of BCBO with three different alcohols are plotted in Figure II.4. All the plots are linear, and the \( R^2 \) values are close to 0.99. It can therefore be concluded that the photochemical reaction of BCBO is first-order, involving the ring opening of BCBO as a rate-determining step to form II-1 and a subsequent faster reaction of II-1 with an alcohol. This reaction mechanism is in accordance with the thermal reactions of benzocyclobutene itself and some cyclobutenones with alcohols.$^{43,45}$

![Figure II.4. Kinetic plots of the photochemical reactions of BCBO with alcohols.](image)

II.3. Conclusion

Benzocyclobutenone is easily prepared in large quantities from the multi-step process using anthranilic acid and 1,1-dichloroethylene or by pyrolysis of \( o \)-toluoyl chloride. The former process gives a reproducible yield (54 %), in a typically 80-g scale.
The pyrolysis process would be more appropriate for a practical production of BCBO, since it does not use any organic solvents and produces a minimal amount of wastes. In addition, the pyrolysis method could be further engineered to become a continuous, high-yielding process.

BCBO reacts readily with primary and secondary alcohols both thermally and photochemically. The thermal reaction proceeds faster with an aromatic alcohol than with an aliphatic alcohol. This difference is negligible when the reaction is performed photochemically.

It has been found that the measured reaction rate exhibits a small inverse correlation with an increase of the solvent polarity. This means that the types of polymers may have some effects on the curing rate, however should not be significant. The photochemical reaction of BCBO with alcohols follows the first-order kinetic with a rate constant in a range of $10^{-4}$ s$^{-1}$ and proceeds via the ring opening of BCBO as the rate-determining step. This result is important and indicates that for cure a BCBO polymer, there is no need to use an excess of alcohols, and indeed the curing time is dependent on the thickness of a polymer film.

II.4. Experimental Section

**Materials:** Anthranilic acid, 1,1-dichloroethylene, propylene oxide and 1-butanol were received from Aldrich Chemical Co. and used without purification. 1-Octanol, 2-octanol and benzyl alcohol were purchased from Fisher Scientific Co. and were used as received.
Characterization: Melting points were taken on a Fisher-Johns melting point apparatus and are uncorrected. Infrared measurements were performed on a Bomem-FTIR Michelson instrument with a resolution of 4 cm\(^{-1}\). The UV-visible range absorption spectra of the polymer films were recorded on a Varian Cary 3 Spectrophotometer. The \(^1\)H NMR and \(^{13}\)C NMR spectra were recorded on either a Varian Gemini-200 or a Bruker-400 instrument and results are reported in ppm from tetramethyldisilane on the \(\delta\) scale. The coupling constants were assigned by assuming that first order spectrum obtained. Low resolution mass spectra were obtained on a DuPont 21-492B spectrometer. The UV light source is from the Novacure spot curing system (EFOS Canada) with a wavelength range of 300 – 350 nm and a light intensity of 1000 mw/cm\(^2\).

Benzocyclobutenone

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

In a 2L beaker placed in an ice bath, anthranilic acid (41.5 g) was dissolved in absolute ethanol (495 mL) and concentrated hydrochloric acid (33 mL). Isoamyl nitrite (82 mL) was added to the stirred solution, followed by addition of diethyl ether (495 mL) after 15-minute stirring. After another 10 minutes, the resulting diazonium salt was isolated by vacuum filtration and rinsed with diethyl ether (165 mL). The diazonium salt was left on the filter funnel for 30 minutes. (Caution! The salt is explosive when completely dry). The diazonium salt (52.6 g), propylene oxide (39.5 mL) and freshly distilled 1,1-dichloroethylene (187 mL) were placed in a dry 2 L round-bottomed flask
equipped with a condenser and nitrogen inlet/outlet. The reaction mixture was gently heated at 40-50 °C for 20 hours and then cooled to room temperature. The tan precipitate was removed by filtration and the brown filtrate containing 2,2-dichlorobenzocyclobutene was concentrated. The oily residue was vacuum distilled to give pure dichlorobenzocyclobutene: IR (NaCl, cm⁻¹) 2942, 683; ¹H NMR (200 MHz, CDCl₃) δ 7.38 (m, 3H), 7.28 (d, 1H, J₉-H = 26 Hz), 4.14 (s, 2H); ¹³C NMR (50 MHz, CDCl₃) δ 198.63, 132.22, 129.31, 124.25, 120.75, 57.63; MS (EI, m/e, relative intensity %) 172 (M⁺, 28.1), 137 (M⁺-Cl, 100), 102 (M⁺-2Cl, 50).

The crude dichloro compound was refluxed for 24 hours with aqueous sulfuric acid (3 wt.%). After the reaction mixture was cooled to room temperature, the crude product was extracted with diethyl ether (4 x 80 mL). The organic layers were combined and washed with saturated KHCO₃ solution (80 mL), and dried over magnesium sulfate. The ether solution was concentrated and the oily residue was distilled under vacuum to give benzocyclobutenone as a colorless liquid (18.5 g, 54.8%); bp₀.₀5 35-37 °C; IR (NaCl, cm⁻¹) 1781, 1758, 1585, 958; ¹H NMR (400 MHz, CDCl₃) δ 7.53 (m, 2H), 7.40 (dt, 1H, J₉-H = 7.9 Hz, J₆₈-H = 0.8 Hz), 7.33 (d, 1H, J₉-H = 7.6 Hz ), 3.97 (s, 2H); ¹³C NMR (50 MHz, CDCl₃) δ 188.54, 151.28, 147.97, 135.17, 128.70, 123.71, 120.48, 52.34; UV (λ_max. nm, CH₂Cl₂) 242, 288; MS (EI, m/e, relative intensity %) 118 (M⁺⁺, 96), 90 (M⁺⁺-CO, 100).

**General procedures for thermal and photochemical reactions of BCBO with alcohols**

**Thermal Reaction:** Benzocyclobutenone and an alcohol were placed in a sealed tube under nitrogen and reduced pressure (20 mmHg). The sealed tube was immersed in
an oil bath at 180-210 °C. The same reaction mixture was placed in a test tube with a stopper so as to follow the reaction. After cooling, the sealed tube was cut and the product was analyzed by NMR without purification.

**Photochemical Reaction**: BCBO and an alcohol were placed in a sealed UV cell (either in solution or in neat) and subsequently UV irradiated at ambient temperatures. The reaction was monitored by GC. The products were characterized as obtained or after removal of the solvent used.

**II-3a (using 1-octanol)**: Colorless liquid; IR (NaCl, cm⁻¹) 2930, 1720, 1255; ¹H NMR (200 MHz, CDCl₃) δ 7.91 (dd, 1H, J₈-H = 8.0 Hz, ⁴J₈-H = 1.5 Hz), 7.40 (dt, 1H, J₈-H = 7.3 Hz, ⁴J₈-H = 1.7 Hz), 7.25 (m, 2H), 4.30 (t, 2H, J₈-H = 6.6 Hz); 2.60 (s, 3H), 1.77 (q, 2H, J₈-H = 7.8 Hz), 1.30 (bs, 10H), 0.89 (t, 3H, J₈-H = 6.7 Hz); ¹³C NMR (50 MHz, CDCl₃) δ 168.03, 140.27, 132.05, 131.90, 130.77, 130.25, 125.92, 65.18, 32.07, 29.48, 29.01, 26.39, 22.92, 22.03, 14.37; MS (EI, m/e, relative intensity %) 248 (M⁺⁺, 8.0), 136 (M⁺⁺-C₆H₁₄, 100), 119 (M⁺⁺-OC₆H₁₅, 66.6), 91 (119-CO, 48.2).

**II-3b (using 2-octanol)**: Colorless liquid; IR (NaCl, cm⁻¹) 2924, 1718, 1256; ¹H NMR (200 MHz, CDCl₃) δ 7.91 (dd, 1H, J₈-H = 8.1 Hz, ⁴J₈-H = 1.4 Hz), 7.40 (dt, 1H, J₈-H = 7.5 Hz, ⁴J₈-H = 1.3 Hz), 7.26 (m, 2H, J₈-H = 7.3 Hz), 5.17 (h, 1H, J₈-H = 6.3 Hz); 2.62 (s, 2H), 1.7 (m, 2H), 1.36 (d, 3H, J₈-H = 6.3 Hz), 1.3 (m, 8H), 0.90 (t, 3H, J₈-H = 6.9 Hz); ¹³C NMR (100 MHz, CDCl₃) δ 167.43, 139.80, 131.64, 131.60, 130.52, 130.36, 125.65, 71.54, 36.11, 31.76, 29.19, 25.48, 22.60, 21.74, 20.10, 14.07; MS (EI, m/e, relative intensity %) 248 (M⁺⁺, 7.1), 163 (M⁺⁺-C₆H₁₃, 1.2), 136 (M⁺⁺-C₆H₁₆, 96.8), 119 (M⁺⁺-
OCH₃ (100), 91 (M⁺⁺-C₅H₉O₂, 41.8); HRMS Calculated for C₁₆H₂₄O₂: 248.1770, Found: 248.1749.

II-3d (using benzyl alcohol): Colorless liquid; IR (KBr, cm⁻¹) 1716, 1251; ¹H NMR (400 MHz, CDCl₃) δ 7.95 (dd, 1H, Jₖ₋ₖ = 8.2 Hz, ⁴Jₖ₋ₖ = 1.3 Hz), 7.20 to 7.45 (m, 8H), 5.33 (s, 2H), 2.60 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 167.34, 140.34, 136.11, 132.06, 131.69, 130.67, 129.69, 128.57, 128.18, 126.97, 125.70, 66.49, 21.80.

II-3f (using 1-butanol): Colorless liquid; IR (NaCl, cm⁻¹) 2960, 1719, 1255; ¹H NMR (400 MHz, CDCl₃) δ 7.90 (d, 1H, Jₖ₋ₖ = 8.1 Hz, ⁴Jₖ₋ₖ = 1.4 Hz), 7.38(dt, 1H, Jₖ₋ₖ = 7.5 Hz, ⁴Jₖ₋ₖ = 1.3 Hz), 7.26 (m, 2H, Jₖ₋ₖ = 7.3 Hz), 5.17 (h, 1H, Jₖ₋ₖ = 6.3 Hz); 2.62 (s, 2H), 1.7 (m, 2H), 7.24(m, 2H), 4.30 (t, 2H), 2.60 (s, 3H), 1.75 (q, 2H), 1.48 (h, 2H, Jₖ₋ₖ = 6.3 Hz), 0.98 (t, 3H, Jₖ₋ₖ = 6.9 Hz); ¹³C NMR (100 MHz, CDCl₃) δ 167.82, 140.02, 131.82, 131.66, 130.52, 130.01, 125.68, 64.64, 30.80, 21.75, 19.36, 13.77; MS (EI, m/e, relative intensity %) 192 (M⁺⁺, 24.8), 136 (M⁺⁺-C₄H₈, 66.4), 119 (M⁺⁺-C₄H₉O, 100), 91 (M⁺⁺-C₅H₉O₂, 52.9); HRMS Calcd. for C₁₂H₁₆O₂: 192.1150, Found: 192.1136.
II.5. References


CHAPTER III. SYNTHESIS AND CHARACTERIZATION OF BCBO POLYMERS

III.1. Functionalization of Benzocyclobutenone

In order for benzocyclobutenone to be incorporated into a polymer system, it first has to be functionalized. Benzocyclobutenones with substituents such as methyl, methoxy, chloro groups on the benzene ring, have been prepared from the corresponding substituted anthranilic acid.\(^1\) The presence of substituents like hydroxyl, amino and nitro groups would be useful for incorporation of BCBO into polymers. However, the synthesis of the nitro BCBO could not be done by direct pyrolysis due to thermal decomposition of the nitro group. In addition, the hydroxyl or amino BCBO cannot be prepared from the corresponding substituted anthranilic acid, as these functional groups would react with the benzyne intermediate. Since benzocyclobutenone is readily available now, direct functionalization of BCBO seems to be the best route.

III.1.1. Synthesis of 5-Aminobenzocyclobutenone

Electrophilic nitration of benzocyclobutenone is expected to produce two isomeric products (Figure III.1). The methylene group directs the ortho and para substitutions and the carbonyl is a meta directing group. Thus, the cyclobutenone unit will direct the electrophilic substitution at positions 3 and 5. However, the 3-substituted BCBO is only a minor product in nitration. In comparison, the electrophilic substitution of benzocyclobutene (BCB) was predicted to occur at positions 3 and 4, but only
substitution at position 4 was observed.\textsuperscript{2} This differs greatly from the prediction based on \textit{o}-xylene which is comparable to BCB from a steric and electronic point of view.

![Chemical structures](image)

\textbf{Figure III.1.} Anticipated substitution positions of some substituted benzenes.

Nitration of benzocyclobutene (Scheme III.1) was first carried out in concentrated sulfuric acid. The nitration gave only mono nitrated products when being carried out between -20 and 0 °C. 5-Nitrobencocyclobutene (nitro-BCBO, \textbf{III-1}) was the major product of the reaction. Varying the reaction temperature from -20 to 0 °C did not affect the reaction yield. After work-up and recrystallization from methanol, \textbf{III-1} was obtained in 83 % yield.

The nitration was also done using nitric acid in acetic anhydride/chloroform, which was slower (24 hours) than the one done in concentrated sulfuric acid (20 minutes). The product \textbf{III-1} was obtained in 73 % yield.
Scheme III.1. Nitration of benzocyclobuteneone.

Nitro-BCBO III-1 was fully characterized by spectroscopic means. The IR spectrum showed the presence of the ketone carbonyl at 1785 cm\(^{-1}\) and as well the nitro group at 1342 and 1522 cm\(^{-1}\). The \(^1\)H NMR spectrum displayed a splitting pattern typical for a mono-substituted BCBO. The \(^13\)C NMR spectrum exhibited only seven peaks. However the intensity of one of the quaternary carbon peaks was unusually high, implying the overlapping of two quaternary carbon peaks. The high-resolution mass spectrum also confirmed the molecular mass of III-1.

Aminobenzocyclobuteneone is a key compound for incorporation of BCBO into polymers, which in principle can be coupled with the carboxylic acid, acyl chloride or anhydride, and isocyanate groups presented in polymers.

Reduction of III-1 in aqueous ethanol with iron and hydrochloric acid yielded 5-aminobenzocyclobuteneone (amino-BCBO, III-2) in good yield (Scheme III.2). The reaction was usually complete within one hour.

Scheme III.2. Reduction of nitro-BCBO (III-1) to amino-BCBO (III-2).
Amino-BCBO was fully characterized. The IR spectrum showed a ketone carbonyl at 1744 cm\(^{-1}\) as well as N-H stretching of a primary amine at 3466 and 3362 cm\(^{-1}\). The \(^1\)H NMR spectrum exhibited a singlet at 3.83 ppm corresponding to the methylene moiety. The aromatic protons had an integral of three and the splitting pattern was in accord with the mono-substituted BCBO. The \(^{13}\)C NMR spectrum displayed eight peaks, corresponding to all the chemically non-equivalent carbons. Finally, the mass for III-2 found in the high-resolution mass spectrum (133.0527) matched well with the calculated one (133.0526).

III.1.2. Synthesis of BCBO Vinyl Monomers

A vinyl monomer, BCBO methacrylate (III-3), was synthesized from methacryloyl chloride and amino-BCBO (III-2) in the presence of triethylamine in tetrahydrofuran (THF) (Scheme III.3). Monomer III-3 was obtained as beige flakes after recrystallization from ethanol/cyclohexane.

\[
\begin{align*}
\text{III-2} & \quad + \quad \text{CH}_3\text{Cl} \quad \xrightarrow{\text{NEt}_3, \text{THF, RT}} \quad \text{III-3} \\
\end{align*}
\]


The structure of monomer III-3 was verified by spectroscopic means. The IR spectrum showed the presence of the cyclobutenone unit (C=O 1745 cm\(^{-1}\)) as well as that
of the amide group (C=O 1766 cm\(^{-1}\), N-H 3357 cm\(^{-1}\)). The \(^1\)H NMR spectrum displayed two vinylic protons and a methyl peak in addition to the peaks from the BCBO moiety. The mass spectrum exhibited a molecular mass of 201, as well as the fragmentation product (m/e 173) resulting from the loss of carbon monoxide.

III.2. Incorporation BCBO into Polymers

There are two general methods for incorporating BCBO into a polymer system. Using compound III-3, BCBO can be incorporated into a wide spectrum of vinyl polymers as a pendant group by homopolymerization and copolymerization with other vinyl monomers. In addition, III-2 can be grafted onto the anhydride- and carboxylic acid-containing polymers via imidization and amidization reactions.

III.2.1. Synthesis of BCBO Polymers by Copolymerization

A convenient way to introduce the benzocyclobutenone group is by free radical polymerization of monomer III-3 with commercially available vinyl monomers such as styrene and methacrylates. Thus, styrene-BCBO copolymers were prepared by radical polymerization using 2,2'-azobisisobutyronitrile (AIBN) as a radical initiator (Scheme III.4). A THF solution of monomer III-3, styrene and AIBN was first deoxygenated with argon, then placed in a sealed reaction vessel and heated at 60 °C for 24 hours. The resulting polymer was precipitated in hexane or methanol. The remaining unreacted monomer was removed by successive precipitations in methanol, as monitored by gel permeation chromatography (GPC). The BCBO content in copolymers was varied by changing the ratio of III-3 to styrene.
Scheme III.4. Copolymerization of monomer III-3 with styrene.

The successful incorporation of monomer III-3 into copolymers III-4 (BCBO-PSi) was indicated by the presence of two carbonyl peaks at 1765 cm\(^{-1}\) for the ketone and 1680 cm\(^{-1}\) for the amide in their IR spectra (Figure III.2). The \(^1\)H NMR spectrum also proved the incorporation of monomer III-3 into the copolymers. Despite the overlap of most peaks arising from monomer III-3 by those of polystyrene, the characteristic methylene peak of BCBO at 3.9 ppm was clearly identified.

Three copolymers were prepared using different feed ratios of monomer III-3 and styrene. The BCBO content in copolymers III-4 was determined by \(^1\)H NMR spectrum, which indicated that 80\% of monomer III-3 was incorporated into polymer III-4a, 97\% into polymer III-4b, and 84\% into polymer III-4c.
Figure III.2. IR spectra of monomer III-3 and polymer III-4b.

The results of thermal analyses on polymers III-4 are summarized in Table III.1. The decomposition temperature of both copolymers was identical to that of polystyrene. Thus, the incorporation of monomer III-3 did not influence the thermal stability of the copolymer.
Table III.1. Thermal properties of polymers III-4.

<table>
<thead>
<tr>
<th></th>
<th>BCBO content (mol%)</th>
<th>T_d (°C)</th>
<th>T_g (°C)</th>
<th>T_RO (°C)</th>
<th>T_g' (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polystyrene</td>
<td>0</td>
<td>378</td>
<td>100</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>III-4a</td>
<td>4.0</td>
<td>376</td>
<td>105</td>
<td>300</td>
<td>129</td>
</tr>
<tr>
<td>III-4b</td>
<td>9.7</td>
<td>372</td>
<td>112</td>
<td>298</td>
<td>140</td>
</tr>
<tr>
<td>III-4c</td>
<td>12.6</td>
<td>371</td>
<td>128</td>
<td>300</td>
<td>155</td>
</tr>
</tbody>
</table>

* Calculated from the peak integration of the ¹H NMR spectrum. * b Onset temperature for 5% weight loss as assessed by TG at a heating rate of 10 °C/min under a nitrogen flow of 200 mL/min. * c First DSC scan at a heating rate of 10 °C/min under a nitrogen flow of 50 mL/min. * d Ring-opening temperature measured at the maximum height of the exothermic peak. * e Second DSC scan at a heating rate of 10 °C/min under a nitrogen flow of 50 mL/min. N/A: Not Applicable.

DSC studies showed the BCBO-PSt partially crosslinked after the first cycle of heating. The first DSC curve exhibited an exotherm peak at about 300 °C due to the ring-opening of the BCBO unit (Figure III.3). On the second scan, the T_g was about 25 °C higher than for the first scan due to the formation of a crosslinked structure. In oscillating DSC, the T_g values of polymers III-4 were detected in the first run, which were higher than that (100 °C) of polystyrene and increased with the amount of BCBO present in the polymer.
Figure III.3. DSC traces of copolymer III-4a.

The proceeding work was extended to the synthesis of terpolymers derived from vinyl monomers, 2-hydroxyethyl methacrylate (HEMA) and BCBO vinyl monomer (III-3) (Scheme III.5). The polymerization was carried out under the same conditions as for the preparation of copolymers III-4. Several series of terpolymers were prepared (see Table III.2).
Scheme III.5. Synthesis of BCBO-containing terpolymers III-5.

The IR spectra of two terpolymers (BMA-HEMA-BCBO III-5a and An-HEMA-BCBO III-5c) are shown in Figure III.4. The IR spectrum of BMA-HEMA-BCBO shows the characteristic peaks at 1732 cm\(^{-1}\) and 1765 cm\(^{-1}\) due to the ester and the BCBO ketone groups, respectively. The cyano group in III-5c appears at 2240 cm\(^{-1}\). The N-H stretch at 3440 cm\(^{-1}\) and N-H bending at 1674 cm\(^{-1}\) for the -CONH- moiety were observed, in addition to a broad OH stretching peak above 3000 cm\(^{-1}\). Thus, terpolymers III-5 contain both BCBO and hydroxyl groups. The NMR spectra further confirmed the incorporation of BCBO as it displays a singlet peak at 4.1 ppm attributed to the methylene protons from BCBO.
Figure III.4. IR spectra of BCBO-containing terpolymers III-5a and III-5c.

The UV spectra of terpolymers III-5 show one peak with a $\lambda_{\text{max}}$ around 320 nm, whose absorptivity is proportional to the feed ratio of the BCBO monomer (Figure III.5). Hence, the BCBO content in the terpolymers can be determined using UV-vis spectroscopic method.
Figure III.5. UV-Vis spectra of terpolymers III-5a1 (5% BCBO) and III-5a4 (10% BCBO).

A standard compound III-6 was used for calibration (Figure III.6). On the basis of this calibration line, the BCBO content in the terpolymers III-5 was easily obtained. It can be seen from Table III.2 that the mole fraction of the BCBO content in the terpolymers is slightly higher than that in the feed.
Figure III.6. Correlation between the BCBO concentration and its absorptivity.

Table III.2. The BCBO and hydroxyl contents and thermal properties of terpolymers III-5.

<table>
<thead>
<tr>
<th>Code</th>
<th>Feed ratio (BCBO mol%)</th>
<th>Feed ratio (OH mol%)</th>
<th>Measured ratio (BCBO mol%)</th>
<th>T_{g1} (^{a}) (°C)</th>
<th>T_{g2} (^{b}) (°C)</th>
<th>T_{max} (^{c}) (°C)</th>
<th>T_{d} (^{d}) (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>III-5a1</td>
<td>5.0</td>
<td>5</td>
<td>7.8</td>
<td>55</td>
<td>55</td>
<td>N/A</td>
<td>250</td>
</tr>
<tr>
<td>III-5a2</td>
<td>5.0</td>
<td>15</td>
<td>6.7</td>
<td>50</td>
<td>50</td>
<td>N/A .</td>
<td>260</td>
</tr>
<tr>
<td>III-5a3</td>
<td>5.0</td>
<td>30</td>
<td>6.9</td>
<td>65</td>
<td>58</td>
<td>N/A</td>
<td>250</td>
</tr>
<tr>
<td>III-5a4</td>
<td>10.0</td>
<td>30</td>
<td>13.2</td>
<td>80</td>
<td>81</td>
<td>N/A</td>
<td>240</td>
</tr>
<tr>
<td>III-5b</td>
<td>5.0</td>
<td>15</td>
<td>7.8</td>
<td>121</td>
<td>112</td>
<td>N/A</td>
<td>246</td>
</tr>
<tr>
<td>III-5c</td>
<td>5.0</td>
<td>15</td>
<td>8.4</td>
<td>90</td>
<td>154</td>
<td>234</td>
<td>270</td>
</tr>
<tr>
<td>III-5d1</td>
<td>5.0</td>
<td>15</td>
<td>7.1</td>
<td>91</td>
<td>126</td>
<td>282</td>
<td>350</td>
</tr>
<tr>
<td>III-5d2</td>
<td>10.0</td>
<td>30</td>
<td>12.1</td>
<td>94</td>
<td>146</td>
<td>299</td>
<td>317</td>
</tr>
<tr>
<td>III-5d3</td>
<td>8.0</td>
<td>24</td>
<td>11.0</td>
<td>94</td>
<td>150</td>
<td>298</td>
<td>337</td>
</tr>
</tbody>
</table>

\(^{a}\) First DSC scan at a heating rate of 10 °C/min under a nitrogen flow of 50 mL/min.  
\(^{b}\) Second scan DSC at a heating rate of 10 °C/min under a nitrogen flow of 50 mL/min.  
\(^{c}\) Ring-opening temperature measured at the maximum height of the exothermic peak.  
\(^{d}\)
Onset temperature for 5% weight loss as assessed by TG at a heating rate of 10 °C/min under a nitrogen flow of 200 mL/min.

Since terpolymers III-5c and III-5d have higher decomposition temperatures than their ring-opening temperatures, the ring-opening events are detectable in first DSC scan. As expected, these exothermic peaks are not observed in second DSC scan (Figure III.7). Also, there should be a significant change in $T_g$ after the first heating due to thermal crosslinking. Accordingly, the $T_{g2}$ should be much higher than $T_{g1}$ as seen for terpolymer III-5c, III-5d1, III-5d2, and III-5d3. For BMA-HEMA-BCBO (III-5a) and MMA-HEMA-BCBO (III-5b) terpolymers, the ring-opening peaks were not observed in the first DSC scan, implying that decomposition occurred before ring opening. Therefore, the $T_g$s for these terpolymers in the first and second scans prior to decomposition temperature (∼240 °C) were unchanged or similar. Polymer III-5a4 had a higher $T_g$ than those of other BMA-HEMA-BCBO terpolymers due to its higher BCBO and hydroxyl contents.
III.2.2. Synthesis of BCBO Polymer by Grafting Reaction

Another method to incorporate BCBO into polymers is to graft amino-BCBO (III-2) into anhydride-containing and carboxylic acid-containing polymers.

Anhydride-containing addition polymers (e.g. polyethylene, polystyrene and polyoctadecene) are commercially available. Via imidization reaction between the amine group from amino-BCBO and the anhydride group in polymers, BCBO can be easily grafted onto these polymers. Thus, poly(maleic anhydride-alt-1-octadecene) was readily converted to BCBO polyoctadecene III-7 by treatment with amino-BCBO in refluxing xylene (Scheme III.6). The BCBO content in these polymers can be tailored by adjusting the feed ratio of amino-BCBO to anhydride group in parent polymers.

Figure III.7. DSC traces of terpolymer III-5c.

The incorporation of BCBO into poly(maleic anhydride-alt-1-octadecene) was evident by the presence of the imide (1776 and 1714 cm\(^{-1}\)), and BCBO (1776 cm\(^{-1}\)), and the disappearance of the anhydride peaks (1870 and 1784 cm\(^{-1}\)) in the IR spectra (Figure III.8) of BCBO polyoctadecene III-7. The aromatic C-H vibration is also seen over 3000 cm\(^{-1}\).
Figure III.8. IR spectra of BCBO polyoctadecene III-7 and its precursor polymer.

The $^1$H NMR spectrum also proved incorporation of amino-BCBO into the polymer. The appearance of signals in the aromatic region confirmed the presence of the BCBO moiety in the polymer. In addition, the characteristic methylene peak around 3.9 ppm was clearly identified. The UV-Vis spectrum also confirmed the incorporation of BCBO ($\lambda_{\text{max}}=320$ nm) into polyoctadecene, since the parent polymer is not absorptive at this wavelength.

Similarly, polyethylene-raft-maleic anhydride (x=98 mol%) was readily converted to BCBO polyethylene (BCBO-PE, III-8) upon imidization with amino-BCBO in the melt at 150 °C. BCBO-PE had a melting point (125 °C by DSC) slightly higher than that (122 °C) of anhydride polyethylene.

The BCBO group can also be incorporated into carboxyl acid (COOH)-containing polymers. The COOH-containing copolyimides are easily made from commercial monomers (e.g. III-9 in Scheme III.8) by one-step solution polymerization in m-cresol at 200 °C.⁴⁻⁶ The incorporation of the BCBO and hydroxyl groups into these polyimides was achieved via the formation of an amide bond from the COOH and amino groups (Scheme III.9). A coupling agent, 1-((3-(dimethylamino)propyl)-3-ethylcarbodiimide (EDC), was used, which gives rise to a water-soluble urea by-product,⁷⁻¹¹ and 1-hydroxy-7-azabenzotriazole (HOAt) was used as a coupling promotor.¹²
The incorporation of BCBO into COOH-PI (III-9) was confirmed by IR. The new peaks at 1687 and 1541 cm\(^{-1}\) are due to the newly formed amide bond (Figure III.9). The disappearance of the broad acid peak is also indicative. The small peak at 3386 cm\(^{-1}\) ascribed to a N-H vibration (from second amide group) is displayed. The \(^1\)H NMR spectrum also confirmed the incorporation of amino-BCBO into the polyimide. The characteristic methylene peak around 4.0 ppm was clearly identified. The peak at 13.9 ppm from COOH disappeared in the \(^1\)H NMR spectrum of III-10. DSC traces (Figure III.10) of BCBO-PI displayed a ring-opening peak at 300 °C, further indicating the incorporation of BCBO into COOH-containing polyimides.

**Figure III.9.** IR spectra of COOH-PI III-9 and BCBO polyimide III-10.
Figure III.10. DSC traces of COOH-PI III-9 and BCBO polyimide III-10 (runs 1 and 2).

III.3. Experimental Section

Materials: Sulfuric acid, nitric acid (70%), nitric acid (90%), iron power, acetic anhydride were purchased from Anachemia. Methacryloyl chloride, 2,2'-azobisisobutylronitrile (AIBN), 4-aminophenethyl alcohol, 3,5-diaminobenzoic acid and other vinyl monomers were purchased from Aldrich Co. All of the vinyl monomers were purified by distillation or chromatography to remove inhibitors and/or impurities Poly(maleic anhydride-alt-1-octadecene) was purchased from Aldrich Co. Polyethylene-graft-maleic anhydride was from DuPont as a brand name of Fusabond®. Both of them were pretreated in an oven at 150 °C prior to use. 4,4'-Hexafluoropropyldene)diphtalic
anhydride and 9,9-bis(4-aminophenyl)fluorene were received from Chriskev Co., and used without further purification.

**Characterization:** See general characterizations on page 48. The polymer samples were analyzed using thermal analysis techniques: Thermogravimetry (TG) and Differential Scanning Calorimetry (DSC). Thermal stabilities, as measured by weight loss, of the polymer samples were determined using a Seiko 120 TG/DTA analyzer from 25 °C to 600 °C at a heating rate of 10 °C/min. The system was permanently purged with 200 mL/min of dry nitrogen. A Seiko DSC 220 was operated at a heating rate of 10 °C/min or at a heating rate of 3 °C/min in the oscillating mode. The system was purged with 50 mL/min of dry nitrogen. Both instruments are calibrated using indium and tin. The apparent molecular weight of the polymers were determined by gel permeation chromatography (GPC) relative to polystyrene standards using chloroform at a flow rate of 1.0 ml/min at ambient temperature.

5-Nitrobenzocyclobutenone (III-1)

![Structure of 5-Nitrobenzocyclobutenone](image)

**Sulfuric acid - nitric acid method:** Benzocyclobutenone (10.10 g, 85.6 mmol) was added slowly to a strongly stirred concentrated sulfuric acid (25 mL), the temperature was maintained between -10 °C and -5 °C. The resulting solution was cooled to -10 °C. The nitration mixture (70 % nitric acid, 8.75 g, 97.2 mmol, in 5 mL of sulfuric acid) which was chilled in an ice bath, was added to the reaction mixture at such
a rate that the solution temperature remained between -10 °C and -5 °C. After the
addition of the nitrating solution, the mixture was stirred for another 10 min at that
temperature. The reaction mixture was then slowly poured into an ice slurry (150 g of ice
in 30 mL of water) with stirring. A yellow product was collected by suction filtration and
washed with water twice, aqueous sodium carbonate solution (10 %) twice, and water
until the rinsing became neutral. The solid product was recrystallized from methanol to
give fine white crystals: 3.44 g (83.1 %).

**Nitric acid (90 %) - chloroform:** Benzocyclobutenone (20.02 g, 169.6 mmol) was
dissolved in chloroform (20 mL) in a round-bottomed flask. Acetic anhydride (40 mL)
was added to the stirring solution. The flask was maintained at room temperature with a
water bath. Nitric acid (90 %, 24 mL) was then slowly added to the stirring solution over a
20-minute period. The temperature was kept below 30 °C. The precipitate was filtered
off, rinsed with water and dried under vacuum. A white precipitate (13.39 g, 48.5 %) was
obtained. More product could be recovered from the filtrate. The washings and the
filtrate were combined and poured into ice water. The mixture was then washed with
water until washings were neutral and then with chloroform. The organic solution was
then dried over MgSO₄ and the solvent evaporated to give an additional 7.35 g of
yellowish solids (75 % overall yield). mp 126-127 °C; IR (KBr, cm⁻¹) 1785, 1522, 1342;

\[ ^1H\text{ NMR (400 MHz, CDCl}_3\] \( \delta \) 8.46 (dd, 1H, \( J_{H-H} = 8.1 \text{ Hz}, \quad 4J_{H-H} = 1.9 \text{ Hz} \)), 8.18 (dd, 1H,
\( 4J_{H-H} = 1.8 \text{ Hz}, \quad 5J_{H-H} = 0.8 \text{ Hz} \)), 7.75 (dd, 1H, \( J_{H-H} = 8.1 \text{ Hz}, \quad 5J_{H-H} = 0.8 \text{ Hz} \)), 4.11 (s, 2H);

\[ ^13C\text{ NMR (100 MHz, CDCl}_3\] \( \delta \) 185.58, 157.02, 149.04, 129.90, 124.70, 115.85, 52.69;

UV (λ<sub>max</sub>, nm, CH₂Cl₂) 231, 167; MS (EI, m/e, relative intensity %) 163 (M⁺⁺, 99.3), 135
(M$^+$-CO, 39.3), 89 (135$^-$NO$_2$, 100); HRMS Calculated for C$_8$H$_7$O$_3$N: 163.0269, Found: 163.0259.

5-Aminobenzocyclobuteneone (III-2)

A suspension of 5-nitrobenzocyclobuteneone (III-1) (5.06 g, 31.0 mmol) and iron powder (5.08 g) in aqueous ethanol (1:1 ratio, 50 mL) was gently refluxed. The acidic aqueous ethanol (1:1 ratio with 6 drops of concentrated hydrochloric acid) was then added to the reaction mixture. A vigorous reflux was maintained for 90 minutes (the reaction should not exceed 3 hours). Addition of hydrochloric acid (2 drops) every 20 minutes was necessary to maintain the reaction rate. Once the reaction was complete, the solution was treated with sodium carbonate (2 g), and was allowed to cool to room temperature. The reaction mixture was passed through a pad of Celite and the iron oxide paste rinsed thoroughly with ethanol. The filtrate was concentrated and the product, a yellow solid, was collected by filtration, rinsed with water and dried under vacuum: 3.81 (92.4 %). mp 92-93 °C; IR (KBr, cm$^{-1}$) 3466, 3362, 1744, 1620; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.30 (d, 1H, J$_{H-H}$ = 7.9 Hz), 6.85 (dd, 1H, J$_{H-H}$ = 7.9 Hz, $^4$J$_{H-H}$ = 2.0 Hz), 6.62 (d, 1H, $^4$J$_{H-H}$ = 1.6 Hz), 3.83 (s, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 188.78, 148.89, 147.46, 141.45, 124.21, 123.04, 104.90, 50.96; UV ($\lambda_{max}$, nm, CH$_2$Cl$_2$) 240, 351; MS (EI, m/e, relative intensity
5-Acetylamidobenzocyclobuteneone (III-6)

\[
\begin{array}{c}
\text{NH} \\
\text{O} \\
\text{O}
\end{array}
\]

A solution of 5-aminobenzocyclobuteneone (III-2) (0.178 g, 1.34 mmol) in acetic anhydride (3 mL) was heated up to 90 °C for 1 hour. Acetic anhydride and acetic acid were removed by vacuum distillation. The residue was then recrystallized twice from chloroform yielding yellow crystals (0.080 g, 34 %). mp 184-185 °C; IR (KBr, cm\(^{-1}\)) 3336, 1744, 1692; \(^1\)H NMR (400 MHz, DMSO-d\(_6\)) \(\delta\) 10.17 (s, 1H), 7.73 (s, 1H), 7.64 (dd, 1H, \(J_{H-H} = 8.0\) Hz, \(J_{H-H} = 1.7\) Hz), 7.60 (d, 1H, \(J_{H-H} = 8.0\) Hz), 3.92 (s, 2H), 2.06 (s, 3H); \(^13\)C NMR (100 MHz, DMSO-d\(_6\)) \(\delta\) 188.13, 168.62, 147.59, 145.75, 140.12, 126.63, 124.31, 109.75 (d), 51.35, 23.98; UV (\(\lambda_{\text{max}}\), nm, CH\(_2\)Cl\(_2\)) 235, 317; MS (EI, m/e, relative intensity %) 175 (\(M^+\), 38.8), 147 (\(M^+\)-CO, 34.4), 105 (\(M^+\)-C\(_3\)H\(_2\)O\(_2\), 100).
BCBO Methacrylate (III-3)

To a solution of amino-BCBO (III-2) (2.556 g, 19.2 mmol) in anhydrous THF (10 ml) at room temperature and under nitrogen, was added triethylamine (2.736 g, 27.1 mmol) in THF (5 ml). The temperature was cooled down to 0 °C and methacryloyl chloride (2.556 g, 32.8 mmol) in THF (10 ml) was added to the solution. The resulting yellow solution was allowed to warm up and was stirred at room temperature overnight. The reaction solution was diluted with diethyl ether (50 ml for 230 mg) and washed with diluted hydrochloric acid three times. Removal of the solvent and subsequent recrystallization of the residue ethanol/cyclohexane afforded the pure amide product as yellow crystalline flakes: (87% yield). mp 147-148 °C; IR (KBr, cm⁻¹) 3357 (N-H), 2923, 1745 (C=O, ketone), 1666 (C=O, amide); ¹H NMR (200 MHz, CDCl₃) δ 7.85 (b, 1H), 7.71 (dd, 1H, J_H-H = 8.1 Hz, 4J_H-H = 1.8 Hz), 7.61 (s, 1H), 7.49 (d, 1H, J_H-H = 7.9 Hz), 5.83 (s, 1H), 5.50 (s, 1H), 3.94 (s, 2H), 2.06 (s, 3H); ¹³C NMR (50 MHz, CDCl₃) δ 167.00, 147.35, 140.77, 138.99, 128.03, 124.42, 120.71, 112.25, 52.06, 19.01; MS (EI, m/e, relative intensity %) 201 (M⁺, 37.5), 173 (M⁺ - CO, 43.5). DSC showed a melting endotherm peaked at 147 °C and an exotherm beginning at 199 °C in the first scan. The second scan displayed no peak up to 330 °C.
Copolymerization of monomer III-3 and styrene

III-4

III-4a (feed ratio: 5 mol % BCBO): To a solution of III-3 (0.201 g, 1.00 mmol) in anhydrous THF (6 ml), were added styrene (1.997 g, 19.0 mmol) and AIBN (0.023 g, 1.0 mol%). The solution was deoxygenated with nitrogen and the vessel was sealed. The solution was stirred at 60 °C overnight. The polymer was then precipitated in hexane. The white powder was purified by three successive reprecipitations from methanol. The polymer was dried under vacuum at 50 °C. GPC (CHCl₃) Mw = 40600, Mn = 22650, Mw/Mn = 1.91; IR (KBr, cm⁻¹) 3026, 2924, 1763, 1601, 1493, 1452; ¹H NMR (400 MHz, CDCl₃) δ (ppm) 7.08 (b), 6.60 (b), 6.48 (b), 3.98 (s), 1.85 (b), 1.45 (b).

III-4b (feed ratio: 10 mol % BCBO): GPC (CHCl₃) Mw = 31080, Mn = 15300, Mw/Mn = 2.03; IR (KBr, cm⁻¹) 3025, 2923, 1762, 1601, 1493, 1452; ¹H NMR (400 MHz, CDCl₃) δ (ppm) 7.08 (b), 6.60 (b), 3.97 (s), 1.85 (b), 1.45 (b).
Terpolymerization of monomer III-3 with hydroxyl ethyl methacrylate (HEMA) and vinyl monomers

![Monomer and Vinyl Monomers Diagram]

General procedure: The terpolymerization reaction was carried out in a vacuum-sealed tube at 60 °C using AIBN as an initiator. The monomer concentration was 2 mol/L approximately in dry THF. The solution was stirred at 60 °C for 24 hours. The polymer product was precipitated into hexane or methanol and dried under vacuum at 50 °C for one day.

**III-5a2** (feed ratio: 5 mol % BCBO, 15 mol % HEMA): GPC (CHCl₃) Mw = 91000, Mn = 39565, Mw/Mn = 2.3; IR (KBr, cm⁻¹) 3523, 3440, 1767, 1727, 1674, 1606, 1479; ¹H NMR (400 MHz, CDCl₃) δ (ppm) 7.50 (b), 6.60 (b), 3.95 (s), 1.91, 1.82 (d), 1.62, 1.40 (d), 1.03, 0.96, 0.87 (t); UV (λ_max, nm, CH₂Cl₂) 255, 309.

**III-5b** (feed ratio: 5 mol % BCBO, 15 mol % HEMA): GPC (CHCl₃) Mw = 84000, Mn = 46667, Mw/Mn = 1.8; IR (KBr, cm⁻¹) 3441, 1765, 1729, 1674, 1606, 1480; ¹H NMR (400 MHz, CDCl₃) δ (ppm) 7.08 (b), 6.60 (b), 3.97 (s), 1.85 (b), 1.45 (b); UV (λ_max, nm, CH₂Cl₂) 250, 320.
III-5c (feed ratio: 5 mol % BCBO, 15 mol % HEMA): GPC (CHCl₃) Mw = 56000, Mn = 35000, Mw/Mn = 1.6; IR (KBr, cm⁻¹) 3533, 2240, 1764, 1728, 1689, 1601, 1535, 1479; ¹H NMR (400 MHz, CDCl₃) δ (ppm) 7.80 (b), 4.24 (b), 3.95 (s), 3.03(s), 2.01(b), 1.96 (b); UV (λmax, nm, CH₂Cl₂) 236, 310.

III-5d1 (feed ratio: 5 mol % BCBO, 15 mol % HEMA): GPC (CHCl₃) Mw = 56183, Mn = 32241, Mw/Mn = 1.6; IR (KBr, cm⁻¹) 3440, 1762, 1721, 1601, 1471; ¹H NMR (400 MHz, CDCl₃) δ (ppm) 7.11 (b), 6.60 (b), 3.97 (s), 1.40 (b); UV (λmax, nm, CH₂Cl₂) 250, 317.

Synthesis of BCBO Polymer III-7

[Diagram of III-7]

In a round-bottomed flask with a condenser under nitrogen, a mixture of poly(maleic anhydride-alt-1-octadecene) (1.0 g, 0.005 mol of anhydride group) and 5-aminobenzocyclobutenone III-2 (0.068 g, 0.005 mol) in xylene were added. The reaction was carried out at the refluxing temperature and monitored by IR. The resulting polymer III-7 was precipitated into methanol and dried under vacuum at 50 °C overnight. GPC (CHCl₃) Mw = 6696, Mn = 4683, Mw/Mn = 1.4; IR (KBr, cm⁻¹) 3026, 1776, 1714,
1614; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ (ppm) 7.60 (b), 7.41(b), 7.08 (b), 4.01 (s), 1.29(s), 0.92(s); UV ($\lambda_{\text{max}}$, nm, CH$_2$Cl$_2$) 250, 320.

Synthesis of COOH-containing Polyimide III-9

![Polyimide III-9](image)

$m:n=2:1$

To a 200 mL three-necked, round-bottomed flask were 4,4'-Hexafluoropropylidene)diphthalic anhydride (4.4425 g, 0.0100 mol), 9,9-bis(4-aminophenyl)fluorene (1.1615 g, 0.0033 mol), 3,5-diaminobenzoic acid (1.0143 g, 0.0067 mol), m-cresol (50 mL), and isoquinoline (10 drops). The reaction mixture was heated to 120 °C and held at this temperature for 2h, then the temperature was elevated to 210 °C (oil bath temperature). The reaction continued for 18h under nitrogen. The solution was cooled to about 100 °C and poured into methanol (400 mL). The whitish polymer was collected by filtration and washed with methanol using a Soxhlet extractor overnight. After drying under high vacuum at 180 °C, III-9 was obtained as white powders: 6.0 g (93.2%). [\eta] = 0.60 dL/g (NMP, 30 °C); IR (KBr, cm$^{-1}$) 1788, 1734, 1602, 1464, 1360, 1259; 1217, 1151. $^1$H NMR (200 MHz, DMSO-d$_6$) $\delta$ (ppm) 13.9 (COOH, s), 8.20-7.20 (aromatic H, b).
Synthesis of BCBO, OH-containing Polyimide III-10

In a round-bottomed flask under nitrogen, polyimide III-9 (1.000 g, 0.017 mmol of COOH), III-2 (0.1131 g, 0.850 mmol), and 4-aminophenethyl alcohol (0.1165 g, 0.850 mmol) in DMF were charged. After 1-hydroxy-7-azabenzotriazole (HOAt) (0.30 g, 2.2 mmol) was added, the reaction mixture was stirred in an ice bath. 1-(3-(Dimethylamino)propyl)-3-ethylcarbodiimide (EDC) (0.42 g, 2.20 mmol) was then added into the polymer solution. The solution was then stirred at room temperature overnight. The resulting BCBO-containing polyimide was precipitated in methanol and dried under vacuum at 50 °C. 1.02 g (91.9 %). [η] = 0.58 dL/g (NMP, 30 °C); IR (KBr, cm\(^{-1}\)) 3366, 1761, 1729, 1681, 1597, 1536, 1478, 1356, 1256; \(^1\)H NMR (400 MHz, DMSO-\(d_6\)) \(\delta\) (ppm) 10.68 (N-H, s), 8.21-7.80 (aromatic H, b), 3.95 (benzyl H, s), 1.85 (b), 1.45 (b); UV (\(\lambda_{max}\), nm, DMF) 240, 300.
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III.4. References


CHAPTER IV. REACTIONS AND POTENTIAL APPLICATIONS OF BCBO POLYMERS

IV.1. Introduction

As demonstrated in Chapter III, the BCBO moiety was successfully incorporated into a variety of polymers. The incorporation of a latent reactive group (BCBO) into polymers enables an ability of tuning the properties of the polymers in a number of ways. Conceivably, both thermal cycloaddition and photoinitiated nucleophilic reaction of BCBO can be applied to BCBO polymers, offering a versatile approach to the synthesis and modification of various polymers (Scheme IV.1). Accordingly, a BCBO-containing polymer

<table>
<thead>
<tr>
<th>BCBO Polymer:</th>
<th>Cycloaddition Reaction</th>
<th>Nucleophilic Reaction</th>
<th>Nucleophilic Reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reaction:</td>
<td>$\text{C}<em>6\text{H}</em>{10}$</td>
<td>$\text{ROH}$ (oligomer / polymer)</td>
<td>$\text{hv}$</td>
</tr>
<tr>
<td>Product:</td>
<td>Grafting of Polymer</td>
<td>Grafting of Polymer</td>
<td>Crosslinked Polymer</td>
</tr>
<tr>
<td>Application:</td>
<td>($C_60$ Polymers)</td>
<td>($\text{Surface Modification}$)</td>
<td>($\text{Direct Photopatterning}$)</td>
</tr>
</tbody>
</table>

Scheme IV.1. Reactions and potential applications of BCBO polymers.

should be able to react with a dienophile such as [60]fullerene ($C_{60}$) and an alcohol. Such a grafting reaction could be controlled in terms of the degree of conversion and occur only at
the surface of the bulk material. If the BCBO and hydroxyl groups are present together in the same polymer chain, a photoinitiated reaction should result in the formation of a crosslinked system in solution or in the solid state. Thus, a direct photopatterning of the BCBO and hydroxyl-containing polymer thin film is highly feasible (Scheme IV.1).

IV.2. Cycloaddition Reaction of BCBO Polymers

Since the development of methods for mass production of [60]fullerene (C60),1 the rich chemistry of C60 has opened an avenue to new materials research and applications.2 Incorporation of C60 into a polymer has been recognized as a simple means of combining the unique electronic, magnetic and optical properties of C60 with macromolecular characteristics such as mechanical strength and good processability.2,3 [60]Fullerene itself can directly be incorporated into a variety of polymers by copolymerization or grafting.4 Chemically functionalized C60 derivatives are either introduced into a condensation polymer through copolymerization or attached onto a polymer by grafting.4,5 When C60 is directly introduced into a polymer, the actual amount of C60 incorporated in the polymer is usually much less than in feed. This consequence necessitates accurate determination of the C60 content in the polymer in order to establish the structure-property relationship. However, there is no general method available for all types of C60 polymers. All the known methods are only suitable for quantification of specific types of C60 polymers, such as thermogravimetry (TG),4d UV-Vis spectroscopy,4b and gel permeation chromatography (GPC),4a or give an estimated value of the C60 content (e.g., from the mass ratio of a reacted monomer and C606). If quantitative incorporation of C60 into a polymer could be achieved through a specific reaction, the quantification of C60 in the resulting C60 polymer may not be needed. For example, a
series of copolyamides containing a controlled amount of C\textsubscript{60} in the main chain were obtained by polycondensation of [60]fullerenebisacetic acid, isophthalic acid and 4,4'-oxydianiline\textsuperscript{7}. Similarly, if the functional group present in a polymer is able to react with C\textsubscript{60} specifically and quantitatively, the polymer containing a known amount of C\textsubscript{60} on the side chain can be obtained. The reaction of an azide with C\textsubscript{60} has been used for this purpose\textsuperscript{8}. The weight percent of C\textsubscript{60} incorporated was found to be slightly less (ca. 80\%) than the theoretical value (i.e. the azide content). Clearly, a functional group that undergoes a high-yield, specific mono-addition reaction with C\textsubscript{60} is desirable.

Upon thermal activation BCBO generates a highly reactive diene (II-1)\textsuperscript{9}, which subsequently undergoes a [4+2] cycloaddition reaction with C\textsubscript{60} (Scheme IV.2)\textsuperscript{10}. Thermolysis of BCBO in refluxing 1,2-dichlorobenzene in the presence of equimolar C\textsubscript{60} afforded the corresponding BCBO-C\textsubscript{60} adduct in 87 \% yield, along with unreacted BCBO.

\begin{align*}
\text{Scheme IV.2. Cycloaddition of benzocyclobutenone with C}_{60}.\end{align*}

It is conceivable that the use of an excess of C\textsubscript{60} could eventually lead to a quantitative conversion of BCBO. If this quantitative reaction could be achieved then the reaction of C\textsubscript{60} with BCBO could be used as a means to incorporate C\textsubscript{60} into polymers in
a quantitative fashion. In this case, BCBO can be used as a handle to link \( C_{60} \) with a polymer and, more importantly, the amount of BCBO present in the precursor polymer can be identical to the \( C_{60} \) content in the resulting polymer. In this thesis, a new route to incorporation of \( C_{60} \) into vinyl polymers (e.g., polystyrene and polyethylene) is demonstrated based on the unique BCBO-\( C_{60} \) cycloaddition chemistry.

IV.2.1. Incorporation of \( C_{60} \) in Polymers via BCBO Group

As mentioned in Chapter III, using monomer III-3, BCBO can be incorporated into a wide spectrum of vinyl polymers as a pendant group through copolymerization.

Free radical polymerization of monomer III-3 and styrene in different feed ratios afforded the copolymers, BCBO-PSt (III-4a-c) (Scheme III.4). The \( C_{60}\)-containing polymers, \( C_{60}\)-PSt (IV-1a-c), were readily obtained from the reaction of BCBO-PSt (III-4a-c) and \( C_{60} \) in refluxing 1,2-dichlorobenzene (Scheme IV.3).

![Diagram showing the incorporation of \( C_{60} \) in polystyrene via BCBO group.]

Scheme IV.3. Incorporation of \( C_{60} \) in polystyrene via BCBO group.
Successful incorporation of C\textsubscript{60} in the polymer was confirmed by a number of spectroscopic means. The FTIR spectra of all C\textsubscript{60}-PSt showed the disappearance of a band at 1765 cm\textsuperscript{-1} due to the BCBO's ketone group (e.g., IV-1a in Figure IV.1). The expected new carbonyl peak attributed to the BCBO-C\textsubscript{60} adduct should be at 1688 cm\textsuperscript{-1} based on the reported properties of a model adduct\textsuperscript{10} (Scheme IV.2). Unfortunately this peak overlapped the amide peak from monomer III-3. The rest of the spectrum is essentially the same as that of the parent BCBO-PSt, except for an additional weak peak at 528 cm\textsuperscript{-1} due to the functionalized C\textsubscript{60} cage in the polymer. The intensity of the peak at 528 cm\textsuperscript{-1} increased gradually with an increase the C\textsubscript{60} content in the polymers (from IV-1a to IV-1c).

![Figure IV.1. IR spectra of BCBO-PSt III-4a and C\textsubscript{60}-PSt IV-1a.](image-url)
Similar to other C\textsubscript{60}-grafted polystyrenes,\textsuperscript{8} all C\textsubscript{60}-PSt had a broad set of resonances between 141 and 148 ppm in their $^{13}$C NMR spectra. The characteristic resonance at 145 ppm for free C\textsubscript{60} was absent in all spectra. The $^{1}$H NMR spectra of C\textsubscript{60}-PSt showed a singlet at 4.80 ppm assigned to the two benzylic protons on the BCBO moiety, which is clearly different from the corresponding protons at 4.0 ppm for BCBO-PSt.

Finally, the presence of C\textsubscript{60} in the polymer chain is evident by its characteristic UV absorption. The UV-Vis spectrum of BCBO-PSt (e.g., III-4a) displayed a peak with $\lambda_{\text{max}}$ near 320 nm (Figure IV.2). However, C\textsubscript{60}-PSt (e.g., IV-1a) had a broad absorption with tailing up to 650 nm, which is beyond the absorption edge of free C\textsubscript{60}. Furthermore, as the amount of C\textsubscript{60} increases from IV-1a to IV-1c, the intensity also increased proportionally (Figure IV.2). It is known that C\textsubscript{60} derivatives show weak or no characteristic absorption ($\lambda_{\text{max}}$ 330 nm) of pure C\textsubscript{60}, depending on the degree of substitution.\textsuperscript{4e}
Figure IV.2. UV-Vis spectra of pure C\textsubscript{60} (1.5 \times 10^{-3} \text{mg/mL}), BCBO-PSt (III-4a, 0.2 mg/mL), and C\textsubscript{60}-PSt (IV-1a-c, 1.6 \times 10^{-2} \text{mg/mL}) in dichloromethane.

GPC analysis indicated that the weight-average molecular weights of C\textsubscript{60}-PSt were slightly higher than those of parent BCBO-PSt (Table IV.1). Moreover, GPC traces of both BCBO and C\textsubscript{60} polymers were mono-modal with nearly equal polydispersity indices (PDI). Therefore, a specific 1:1-addition occurred for C\textsubscript{60} with all the BCBO groups in the precursor polymers III-4, otherwise multiple addition would lead to the production of a much higher molecular weight fraction of C\textsubscript{60} polymers and broader GPC traces or larger polydispersity indices. In other words, this indicates that the reaction was almost quantitative and that cycloaddition occurs with a 1:1 stoichiometry. To further prove the incorporation of C\textsubscript{60} in the polymer, the amount of C\textsubscript{60} in polymers IV-1 was
determined by quantitative UV analysis and compared with the BCBO content in the precursor polymers III-4 (Table IV.1). It was found that molar percent of C\textsubscript{60} and BCBO matched well, except for polymer IV-1c that had the highest C\textsubscript{60} content (44\% by weight).

Table IV.1. Characterization of BCBO- and C\textsubscript{60}-containing polystyrenes.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>BCBO in III-4</th>
<th>C\textsubscript{60} in IV-1</th>
<th>Mw</th>
<th>PDI</th>
<th>T\textsubscript{d}</th>
<th>T\textsubscript{g}</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Wt%\textsuperscript{a}</td>
<td>Mol%\textsuperscript{b}</td>
<td>Wt%\textsuperscript{c}</td>
<td>Mol%\textsuperscript{b}</td>
<td>x 10\textsuperscript{-d}</td>
<td>°C</td>
</tr>
<tr>
<td>III-4a</td>
<td>7.35</td>
<td>3.94</td>
<td>3.97</td>
<td>2.2</td>
<td>376</td>
<td>105</td>
</tr>
<tr>
<td>III-4b</td>
<td>17.3</td>
<td>9.77</td>
<td>3.98</td>
<td>2.1</td>
<td>372</td>
<td>112</td>
</tr>
<tr>
<td>III-4c</td>
<td>21.8</td>
<td>12.6</td>
<td>1.60</td>
<td>1.8</td>
<td>371</td>
<td>128</td>
</tr>
<tr>
<td>IV-1a</td>
<td></td>
<td></td>
<td>22.5</td>
<td>4.18</td>
<td>4.27</td>
<td>2.2</td>
</tr>
<tr>
<td>IV-1b</td>
<td></td>
<td></td>
<td>39.4</td>
<td>9.33</td>
<td>4.16</td>
<td>2.5</td>
</tr>
<tr>
<td>IV-1c</td>
<td></td>
<td></td>
<td>43.8</td>
<td>11.2</td>
<td>1.75</td>
<td>2.0</td>
</tr>
</tbody>
</table>

\textsuperscript{a} Determined by UV analysis at 320 nm. \textsuperscript{b} Calculated from molecular weight of repeat units. \textsuperscript{c} Determined by UV analysis at 330 nm. \textsuperscript{d} Onset temperature for 5\% weight loss, as assessed by TG at a heating rate of 10 °C/min under nitrogen. \textsuperscript{e} Measured by DSC at a heating rate of 10 °C/min under nitrogen. \textsuperscript{f} Transition was too broad to determine a T\textsubscript{g}.

All three C\textsubscript{60}-PSt were readily dissolved at ambient temperatures in common organic solvents such as CHCl\textsubscript{3}, CHCl\textsubscript{2}, and THF, giving rise to a dark brown-purple colored solution. This solubility behavior is similar to polystyrene but unlike C\textsubscript{60} itself, demonstrating the advantage of having a polymer-bonded fullerene for improved processability. Although the thermal stability of C\textsubscript{60}-PSt was comparable to that of polystyrene or BCBO-PSt, as compared by their onset temperatures for 5\% weight loss,
the glass transition temperatures ($T_g$) of C$_{60}$-PSt increased noticeably (Table IV.1). For example, polymer IV-1b containing 9.33 mol % of C$_{60}$ had a $T_g$ of 156 °C, which is about 56 °C higher than that of polystyrene and 44 °C higher than that of its precursor polymer III-4b. With increasing the C$_{60}$ content in C$_{60}$-PSt, the $T_g$ value increased. However, the phase-separation also occurred at the same time when due to the presence of large amounts of C$_{60}$ was present. Therefore, broadening the $T_g$ transition was observed for IV-1c.

The BCBO group can also be incorporated directly into certain functionalized polymers by post polymerization transformation, through which C$_{60}$ can then be introduced. Thus, Grafting of BCBO-PE III-8, derived from the imidization of polyethylene-graft-maleic anhydride and III-2, with an excess of C$_{60}$ was carried out in refluxing 1,2-dichlorobenzene, yielding light brown C$_{60}$-PE IV-2 quantitatively (Scheme IV.4). Incorporation of C$_{60}$ into polyethylene was evident by IR spectroscopy. The IR spectrum of C$_{60}$-PE IV-2 displayed a characteristic band at 528 cm$^{-1}$ due to C$_{60}$ and showed no peak at 1765 cm$^{-1}$ that was seen in the IR spectrum of the starting BCBO-PE III-8 (Figure IV.3). BCBO-PE III-8 had an absorption with $\lambda_{\text{max}}$ at 334 nm. For C$_{60}$-PE IV-2 this peak shifted to 314 nm and a broad absorption appeared at 370-500 nm due to the presence of C$_{60}$. In DSC analyses an exothermic peak was observed at 225 °C for BCBO-PE III-8 due to the ring opening of BCBO but not for C$_{60}$-PE IV-2.
Scheme IV.4. Incorporation of C_{60} in polyethylene via BCBO group.

Figure IV.3. IR spectra of BCBO-PE (III-8) and C_{60}-PE (IV-2).
IV.3. Nucleophilic Reaction of BCBO Polymers

Chemical modification of polymer systems involves the introduction of various functional groups through typical reactions such as grafting and crosslinking. It provides a means to tailor and enhance the bulk and/or the surface properties of existing polymeric materials. In many cases, combined synthesis and post-polymerization (grafting, crosslinking, and chain extension) through a latent reactive group, offers many advantages. BCBO undergoes nucleophilic reactions with alcohols by heating and UV irradiation, besides cycloaddition reactions. In addition, the photochemical reaction offers a convenient means for product modification, especially for surface modification.

IV.3.1. Bulk Grafting with Alcohols

In this work, BCBO-containing polystyrene was chosen to show how it could be grafted through the reaction of BCBO with poly(ethylene glycol) (PEG).

Poly(ethylene glycol) has been used to modify polymer surfaces for biomedical applications. Poly(ethylene glycol)-grafted-polystyrenes (PSt-g-PEG) are widely used as solid support in the preparation of peptide libraries since they are readily processed and are biocompatible. A wide variety of functional groups have been introduced onto polystyrene either by direct electrophilic substitution or from lithiated polystyrene. PSt-g-PEG was prepared from lithiated polystyrene and ethylene oxide. Friedel-Crafts alkylation of polystyrene with propylene oxide in the presence of a Lewis acid catalyst introduced a hydroxy group onto polystyrene. The hydroxylated polystyrene would then react with ethylene oxide to form a PSt-g-PEG. One problem associated with the hydroxylated polystyrene is the formation of polysubstituted benzene ring. The “graft onto” method we
present here does not have this drawback, since the hydroxyl group of poly(ethylene glycol) reacts with BCBO in a polymer to yield the PEG grafted polymer.

Polymers III-4a and III-4b containing 4 and 10 mol % of BCBO (Scheme III.4) was successfully grafted with monohydroxyl-containing PEG, poly(ethylene glycol) methyl ether \([\text{CH}_3(\text{OCH}_2\text{CH}_2)_n\text{OH}]\) in solution at room temperature. BCBO-PSt was dissolved in dichloromethane in an UV cell, followed by addition of a large excess of PEG. The UV cell was irradiated under the UV light (not the spot cure) at a wavelength of 320 nm for a few hours. The reaction was monitored by IR spectroscopy. After the reaction was complete, the grafted polymer was precipitated in water or methanol. The remaining unreacted PEG was washed away using a Soxhlet extractor with methanol. The resulting PSt-g-PEG IV-3a-550, IV-3b-550, IV-3a-2000 and IV-3b-2000 (Scheme IV.5) are named according to the starting copolymers (III-4a and III-4b), and the molecular weight of PEG (Mw=550, 2000).

![Scheme IV.5. Grafting BCBO polystyrenes III-4 with poly(ethylene glycol) methyl ether.](image_url)
The IR spectrum (Figure IV.4) of grafted polymer showed the complete disappearance of the ketone group previously found at 1765 cm\(^{-1}\), and two new peaks at 1730 cm\(^{-1}\) and 1109 cm\(^{-1}\) due to the formation of an ester group, and the presence of ether bonds respectively. The degree of grafting can be controlled by the BCBO content in copolymer, which was confirmed by \(^1\)H NMR (400 MHz). The NMR spectrum of each of the four PST-g-PEG polymers showed a small peak at 2.5 ppm assigned to three protons of the newly formed ester's methyl group, which is clearly different from the corresponding two benzylic protons at 4.0 ppm of the BCBO moiety. Both of these two peaks had the similar integration ratio, implying the nearly completion of the grafting reaction.

Figure IV.4. IR spectra of BCBO-PSt III-4a and PST-g-PEG IV-3a-500.
The results obtained from thermal analyses of the PSt-g-PEG polymers are reported in Table IV.2. The decomposition temperature was not related to the BCBO content but rather depended on the length of the poly(ethylene glycol) side chain. Polymer IV-3a-550 had a lower decomposition temperature than IV-3a-2000. The higher decomposition temperature of IV-3a-2000 and IV-3b-2000 may be due to their higher overall molecular weights.

Table IV.2. Thermal properties of PSt-g-PEG IV-3.

<table>
<thead>
<tr>
<th></th>
<th>$T_d$ a (°C)</th>
<th>$T_g$ b (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>IV-3a-550</td>
<td>335</td>
<td>-14, 41, 149</td>
</tr>
<tr>
<td>IV-3b-550</td>
<td>327</td>
<td>-46, 16, 123</td>
</tr>
<tr>
<td>IV-3a-2000</td>
<td>363</td>
<td>-10, 138</td>
</tr>
<tr>
<td>IV-3b-2000</td>
<td>369</td>
<td>-49, 134</td>
</tr>
</tbody>
</table>

$a$ Onset temperature for 5% weight loss as assessed by TG at a heating rate of 10 °C/min, under a nitrogen flow of 200 mL/min. $b$ From 2nd DSC scan, at a heating rate of 10 °C/min, under a nitrogen flow of 50 mL/min.

The DSC traces obtained for the grafted polymers exhibited a very broad $T_g$ transition from -50 to -10 °C. This is a common phenomenon for branched polymers. All of them showed at least two $T_g$ transitions, the lower one for PEG side chain, the higher for the polystyrene main chain. For IV-3a-550 and IV-3b-550, the two lower $T_g$ transitions may be due to micro-phase separation. However, only one lower $T_g$ could be measured for IV-3a-2000 and IV-3b-2000, since the longer side chain makes the grafted polymers more entangled and thus more miscible. The $T_g$ associated with the polystyrene segments was higher than that (e.g., 100°C) of polystyrene alone. In addition, IV-3b-
2000 had a melting point at 42 °C due to long PEG chain, but IV-3a-2000 did not. This can be explained by the fact that there is not enough PEG side chain in IV-3a-2000 to pack closely enough to form an ordered structure.

IV.3.2. Surface Grafting with Alcohols

Surface modification has become an attractive way to expand and improve the functions of a polymer. Potentially, it can maintain the desirable bulk properties, but changes the surface property, such as biocompatibility, adhesion, permeability and wettability. 16

Polyolefins are rather unreactive hydrocarbon polymers with low surface energy. It is not very wettable with polar solvents, and possesses no reactive functional groups or sites at which hydrogen-bonding or acid-base chemistry could occur. A variety of techniques are used for activation of the polyolefin surface, including acid etching, 17 X-ray irradiation, 18 ultraviolet irradiation, 19 electron beam bombardment, 20 ozone treatment, 21 corona discharge 22 and plasma treatments. 23 The polar groups are generated on the polymer surface as a result of these treatments. The peroxides and hydroxyperoxides, generated during these treatments are capable of initiating radical polymerization of vinyl monomers, resulting in surface-grafted polymer chains. Surface grafting appears to be one of the most versatile and convenient methods to achieve specific properties useful for applications such as enzyme/protein immobilization. The grafting via a covalent bonding with the functional groups is particularly attractive. 24

Photografting through the BCBO group in a polymer can be used for surface modification. The reaction of BCBO with an alcohol or polyol provides a simple way to
modify a variety of polymer films and fibers at their surfaces. Thus, a commercially available 0.2-mm thick polyethylene (PE) film was used as a substrate to demonstrate the surface modification using the BCBO photochemistry. BCBO-containing polyoctadecene III-7 (Scheme III.6) was used as a surface promoter, which was first spin-coated on a PE film, followed by spraying with the hydroxyl-containing PEG \([\text{CH}_3(\text{OCH}_2\text{CH}_2)_n\text{OH}, \text{Mw}=550]\) and UV irradiation (spot cure) for about 1 min at ambient temperature (Figure IV.5). The transformation from III-7 to IV-4 that occurred on surface is shown in Scheme IV.6. After irradiation, an excess of PEG was washed away with methanol and the film was dried under vacuum.

![Hydrophilic PEG, BCBO polyoctadecene III-7, PE film](image)

**Figure IV.5.** Surface modification of polyethylene using the BCBO photochemistry.

\[
\begin{align*}
\text{III-7} & \quad \text{PEG} \quad \text{hv} \quad \text{IV-4} \\
\text{O} & \quad \text{N} & \quad \text{CH}_2\text{CH} \\
\text{CH}_3(\text{CH}_2)_{14}\text{CH}_2 & \quad \text{O} & \quad \text{CH}_2\text{CH} \\
\text{N} & \quad \text{O} & \quad \text{CH}_3(\text{CH}_2)_{14}\text{CH}_2 \\
\text{phenyl} & \quad \text{O(CH}_2\text{CH}_2\text{O})_n\text{CH}_3 & \\
\end{align*}
\]

**Scheme IV.6.** Photografting reaction occurred at the polymer surface.
The ATR-IR (Figure IV.6) confirmed the existence of the BCBO moiety on the PE surface before photografting, with the carbonyl peak at 1762 cm$^{-1}$. In contrast, after photografting, the same peak decreased but did not disappear since an imide group from the BCBO-polyoctacedene is also present. The increase in intensity of the peak at 1721 cm$^{-1}$ demonstrated the ester formation from BCBO and PEG. Furthermore, the broad peak at 1104 cm$^{-1}$ indicated the presence of the PEG segment, further proving the surface grafting.

![ATR-IR spectra](image)

**Figure IV.6.** ATR-IR spectra of the BCBO polymer III-7 coated on the PE film surface before and after photografting with PEG.

The X-ray photoelectron spectroscopic (XPS) studies showed the carbon peak of the BCBO ketone C=O was present (288.2 eV) prior to PEG grafting (Figure IV.7). After
photographing the carbon peaks associated with the ether linkage $\text{C}=\text{O}$ of PEG and carbonyl $\text{C}=\text{O}$ of the ester were seen at 286.4 eV and 289.2 eV, respectively. Moreover, the change in the intensities of the peaks is proportional to the concentration of BCBO and PEG units.

**Figure IV.7.** XPS survey spectra of the BCBO polymer III-7 coated on the PE film surface before and after photografting with PEG.

**Figure IV.8.** UV-Vis spectra of polyoctadecene III-7 (containing BCBO) and IV-4 (containing PEG).
UV-vis spectra of the BCBO modified PE film displayed high absorbance in the range of 280-400 nm. After photografting, the absorbance decreased due to the ring-opening of BCBO (Figure IV.8).

The PEG-grafted PE films is hydrophilic on surface and hydrophobic in bulk. The dye-stain test was performed on the PEG-grafted surface, as shown in Scheme IV.7. The hydrophilic PEG was coated on BCBO-PE surface, followed by UV irradiation through a photo mask. After the excess PEG was washed away, the PE film surface was sprayed with a hydrophilic dye, 3,3'-diethylthiadicarbocyanine iodide in 0.5 wt% aqueous solution. It can clearly be seen that only the area that was exposed to light was grafted with PEG and thus is colored in blue (Figure IV.9). The dye stains shows the location that the photografting has occurred, and indicates an increase in the surface hydrophilicity due to the presence of PEG. Conceivably, by using other functional molecules containing a hydroxyl group, a polymer film can be selectively modified at its surface to have other desirable properties.

**Scheme IV.7.** Surface modification and dye stain test setup.
IV.3.3. Photocurable Vinyl Polymers

The extensive use of crosslinked polymers in industry can be attributed to their excellent stability at elevated temperatures and resistance to mechanical deformation. Although crosslinked polymers are mechanically and thermally very stable, the physical form of these materials can be hard to manipulate, ultimately limiting the versatility of these materials. They are typically available as low molecular weight prepolymer (e.g., bis-acrylates) and synthesized using step-growth methods where the polymer growth and crosslinking arise from the same chemical reaction.\(^{25}\) Curing process involving the use of a prepolymer is often problematic, as a complete cure is rarely achieved and defects due to unreacted chain ends and intramolecular cyclization are common.

Another approach to the crosslinked polymer is to use a curable high polymer as a prepolymer, which would offer the following features. First, the chain-growth and cross-
linking reactions would be independent of one another, providing full control over the chemical structure of the prepolymer. Second, the crosslinking group could be incorporated as a comonomer into the prepolymer, allowing for the control of the degree of crosslinking. It is therefore desirable to design latent reactive monomers that allow linear chain growth and crosslinking to take place in two separate stages.  

The synthesis and characterization of such as monomer and the corresponding prepolymer (III-5) has been described in III.2.1. These polymers should all be capable of undergoing a self crosslinking reaction upon UV irradiation either in solution or in the solid state (Scheme IV.8).

**Scheme IV.8.** Photoinitiated self crosslinking reaction of the BCBO and hydroxyl-containing polymers.
Thus, 15 - 20 wt % solutions of III-5a1 in chloroform were UV irradiated using the EFOS spot light curing system with the light intensity of 500 mW/cm² at wavelength 320 nm. As shown in Scheme IV.8, the polymers were self crosslinked because of the nucleophilic reaction of BCBO and hydroxyl groups in the polymer chain. The solution of polymer III-5a1 was fluid before UV curing (photograph a, Figure IV.10). The gel formation occurred after one-minute irradiation (photograph b, Figure IV.10). Photograph c shows the pieces of gels after being broken with an object.

Figure IV.10. Photographs of (a) polymer III-5a1 in chloroform solution, (b) the gel formed immediately after UV curing, and (c) gel after being broken.
BCBO-containing terpolymers III-5 can also be cured in the solid state by UV irradiation. The chloroform solution of polymer III-5a1 was spin coated on a NaCl plate. The film was cured by UV light (intensity 500 mw/cm²) while being monitored by IR. Figure IV.11 shows the IR spectra of terpolymer III-5a1 being cured at different times. Before UV curing, the peak at 1765 cm⁻¹ due to BCBO ketone group was intense, but decreased noticeably with increasing the UV curing time.

![Graph showing IR spectra at different times](image)

**Figure IV.11.** IR spectra of terpolymer III-5a1 at different UV curing time.
A typical UV-vis spectrum of a thin film of terpolymer III-5a1 at a given time of irradiation is shown in Figure IV.12. The maximum absorbance at 320 nm decreased with an increase in the irradiation time, indicating that the photochemical reaction of BCBO group via the ketene intermediate with a hydroxyl group proceeded in a time-dependent manner to form an ester group. Moreover, as the curing extent or degree of cross-linking increased, the peak became smaller, the shape changed and eventually blue shifted to approximate to 295 nm when the UV curing closed to complete, due to the loss of the aromaticity upon ring-opening. The curve 1 in Figure IV.12 is the UV spectrum of completely cured sample III-5a1 as determined by IR. This preliminary result shows that the curing reaction of BCBO with a hydroxyl group in terpolymers at thin film state occurs very fast, and completes in less than one minute.

![UV-Vis spectra of terpolymer III-5a1 at different UV curing time.](image)

**Figure IV.12.** UV-Vis spectra of terpolymer III-5a1 at different UV curing time.
IV.3.4. Photocurable Polyimides

Aromatic polyimides are high performance materials due to their excellent electrical, and thermal properties and their thermal stability, and are being used in a number of industrial sectors. In recent years, photocurable polyimides have received much attention, in particular as a circuit framing material and as an electrical insulation membrane between layers of integrated circuits. In the field of electronics, polyimide films made from the precursor poly(amic acid) by thermal cure have also been used for pattern formation in the production of printed circuit boards. However, the etching process involves the use of harmful hydrazine. The problems can be circumvented by using photocurable polyimides. Several types of photocurable or photosensitive polyimides and their precursors have been investigated.

Kerwin and Goldrick first reported the use of photosensitive polyimides, which includes poly(amic acid) and sodium dichromate as a photoreactive additive. The application of this material to electronic devices is problematic as a result of the instability of the prepolymer solution and the unavoidable contamination with residual chromic ions. The first polyimide material applicable to microelectronics device fabrication was reported by Rubner et al. They described the use of negative-type photosensitive polyimide precursors, in which a photoreactive methacrylol group was introduced to the polymer side chain by esterification of the carboxyl groups present in a poly(amic acid). Alternatively, Yoda and Hiramoto demonstrated a different way of introducing the photoreactive groups. In their materials, an amino compound with a photoreactive methacrylol group was added to a poly(amic acid) solution as a photoreactive additive. The methacrylol group is incorporated by the formation of a salt
between the amino group of the photosensitive additive and the carboxylic acid group of the poly(amic acid). Kataoka et al. described the synthesis of a highly photosensitive material containing aromatic azide compounds as a photosensitive additive.\textsuperscript{37,38}

However, the polyimides containing the radical-generating groups have a major problem associated with radical quenching, because the radical polymerization is inevitably inhibited by atmospheric oxygen. Recently, photoinitiated cationic polymerization has become a candidate for a new UV curing system, because there is an advantage in this method for which the reaction is not inhibited by atmosphere oxygen.\textsuperscript{39} Cationic polymerizable groups such as epoxy\textsuperscript{40} or vinyl ether groups\textsuperscript{41} have been introduced into photosensitive polyimides by polymer transformations. However, it is difficult to introduce these functional groups into the polymer selectively and quantitatively.

There is a great interest in fully imidized, photocurable polyimides that offer lower shrinkage (< 20 %) and do not need curing temperatures as high as 300 °C for the current systems. Only a few examples have been reported to date.\textsuperscript{42-48} Soluble, photosensitive polyimides containing benzophenone and thioxanthone chromophores were reported by Pfeifer and Rhode in 1985. In this case, the formation of a crosslinked network does not generate any volatile by-products. The polyimides containing a carboxylic acid group has been converted into a photoreactive polyimide by transforming the acid group to a methacrylate group.\textsuperscript{43}

In our work based on the BCBO chemistry, a carboxylic acid-containing polyimide can be readily converted into a photocurable polyimide by incorporating a BCBO group into the system.
IV.3.4.a. Self Photocurable BCBO Polyimide

Since BCBO reacts with a hydroxyl group upon UV irradiation, the polyimide III-10 should be photoreactive by itself as it contains the BCBO and hydroxyl groups. As shown in Figure IV.13, the solution of III-10 became a gel after UV irradiation for 1 minute (intensity: 500 mW/cm²), without using a catalyst or a photoinitiator.

![Photographs of polymer III-10 in chloroform (a) and the gel formed after UV irradiation (b).](image)

Figure IV.13. Photographs of polymer III-10 in chloroform (a) and the gel formed after UV irradiation (b).

The polymer III-10 also undergoes the photoinitiated crosslinking in the solid state. A thin film of III-10 was spin coated on a NaCl plate, and UV cured for 2 minutes. As shown in Figure IV.14, the peak at 1767 cm⁻¹ due to imide and BCBO decreased,
while the peak at 1736 cm$^{-1}$ increased as a result of the formation of an ester group. However, not all the BCBO group in the polymer reacted in this case.

![IR spectra of BCBO polyimide III-10 before and after UV curing.](image)

**Figure IV.14.** IR spectra of BCBO polyimide III-10 before and after UV curing.

The UV curing improved the thermal stability of polyimide III-10 as assessed by TG (Figure IV.15). The temperature for 5% weight loss for III-10 after cure was 413 °C, which is twenty degrees higher than that of before cure.
Figure IV.15. TGA thermograms of polyimide III-10 before and after UV cure.

The film of polyimide III-10 on a quartz plate was UV cured, as monitored by UV-vis spectroscopy (Figure IV.16). After cure, the shoulder peak around 300 nm became flatter and the peak at 230 nm decreased with an increase in cure time.
Figure IV.16. UV-Vis spectra of BCBO polyimide III-10 being cured at different times.

IV.3.4.b. Direct Photopatterning of BCBO Polyimide

As mentioned before, the chloroform solution of III-10 was UV irradiated and a transparent gel was readily formed (Figures IV.13). This result indicates that the photocurable polyimide III-10 can be used to directly pattern substrates. Thus, a thin film was deposited on a silicon wafer by spin coating a solution of III-10 (10 wt % in tetrachloroethane). After UV cure through a contact mask for 2 minutes (wavelength range 300–350 nm, intensity 500 mW/cm²), the image was developed after simple washing in chloroform (Figure IV.17).
Figure IV.17. A photopatterned image using BCBO polyimide III-10 (500 times magnification).

It is worthwhile noting that the patterns are readily formed without going through a baking process, which is essential for the conventional photoresist materials. The scanning electron micrographs (SEM) (Figure IV.18) display the dark areas for the cured polyimide materials and white lines with a 3 μm width for the silicon wafer.

A Dektak surface profiler was used to mechanically verify the pattern structure and dimensions. Figure IV.19 displays the depth profile of five white strips shown in Figure IV.18. The peak distance is in agreement with the line width of the mask used. It shows that the average size of the hills and valleys of the photopatterned image are approximately 700 nm in depth.
Figure IV.18. SEM photographs of a photopatterned structure of BCBO polyimide III-10.

Figure IV.19. Dektak profile of the photopattern shown in Figure IV.18.
IV.4. Experimental Section

**Materials:** C<sub>60</sub> (99.99 % purity) was purchased from Materials and Electrochemical Research Company, Tucson, USA. Poly(ethylene glycol) methyl ethers (M<sub>w</sub> = 500 and 2000), 3,3′-diethylthiadicarbocyanine iodide, 1,2-dichlorobenzene, and other solvents were purchased from Aldrich, and used as received.

**Characterization:** See general characterizations on pages 48 and 78. ATR-IR was performed on a Bomen FTIR Michelson series instrument using a crystal of ZnSe with a dimension of 50 x 20 x 2 mm and 45° of θ. X-ray photoelectron spectrometer (XPS) analysis was done at the National Research Council of Canada in Ottawa. The sample surface was analyzed using a KRATOS AXIS HS. The size of the analyzed area was about 1 mm<sup>2</sup>. Monochromatized Al Kα radiation was used for excitation and a 180° hemispherical analyzer with a three channel detector was employed. The X-ray gun was operated at 15 kV and 20 mA. The spectrophotometer was operated in Fixed Analyzer Transmission mode (FAT) throughout the study using electrostatic magnification. Survey and high resolution spectra were collected using 160 and 20 eV pass energy respectively. The pressure in the analyzer chamber was 10<sup>-8</sup> to 10<sup>-9</sup> torr. An electron flood gun was used to neutralize the charge during the experiment. In order to verify that the surfaces were not damaged during angle dependent studies, the surfaces were scanned at zero degree take-off angle both before and after the angle dependence measurements. Binding energies were referenced to the carbon-carbon bond which was assigned a binding energy of 285 eV. Atomic composition was estimated using standard software
provided with the instrument and using the following sensitivity factors: 0.25 for Cls, 0.66 for Ols and 0.42 for Nls relative to Fls at 1.00.

**Photocuring:** The UV irradiation was carried out statically at given exposure times. The Novacure spot curing system from EFOS in Canada was used. With a built-in radiometer and a dual bi-directional shutter, the light intensity and exposure time can be precisely selected. In this study, the wavelength range of 300-350 nm and light intensity of 500 mW/cm² were chosen. A 100 Mw mercury lamp (UVP, B-100) with a beam light centered at 320 nm was also used for the photocuring.

**Synthesis of C₆₀-PSt (IV-1)**

![Chemical structure of C₆₀-PSt](image)

In a typical run, a three-necked flask was charged with 100 mg of BCBO-PSt III-4, 100 mg of C₆₀, and 10 mL of 1,2-dichlorobenzene. The resulting purple solution was then heated to reflux under nitrogen and the reaction was monitored by IR and GPC. After 3 hours, the mixture was poured into hexane to give brown solids. The solids were dissolved in toluene and precipitate from hexane again. The same purification process
was repeated several times until no more free C₆₀ could be detected. After drying at 50°C in vacuo for 24 hours, polymer IV-1 was obtained as brown powders.

**IV-1a** (4.18 mol % of C₆₀): GPC (CHCl₃) Mw = 42700, Mn = 19409, Mw/Mn = 2.2; IR (KBr, cm⁻¹) 1765, 1688, 1600, 1493, 528; ¹H NMR (400 MHz, CDCl₃) δ (ppm) 7.06 (b), 6.60 (b), 4.76 (s), 1.85 (b), 1.45 (b); ¹³C NMR (100 MHz, CDCl₃) δ (ppm) 186.25, 145.56, 127.96, 127.68, 125.67, 77.34, 77.02, 76.71, 40.37, 21.98; UV (λ max, nm, CH₂Cl₂) 256, 320 (w).

**IV-1b** (9.33 mol % of C₆₀): GPC (CHCl₃) Mw = 41600, Mn = 16640, Mw/Mn = 2.5; IR (KBr, cm⁻¹) 1764, 1688, 1600, 1493, 527; ¹H NMR (400 MHz, CDCl₃) δ (ppm) 7.06 (b), 6.61 (b), 4.76(s), 1.86 (b), 1.46 (b); ¹³C NMR (100 MHz, CDCl₃) δ (ppm) 186.32, 145.58, 128.02, 127.62, 125.71, 77.33, 77.02, 76.70, 40.39, 21.95; UV (λ max, nm, CH₂Cl₂) 250, 320 (w).

**IV-1c** (11.2 mol % of C₆₀): GPC (CHCl₃) Mw = 17500, Mn = 8750, Mw/Mn = 2.0; IR (KBr, cm⁻¹) 1765, 1688, 1600, 1493, 528; ¹H NMR (400 MHz, CDCl₃) δ (ppm) 7.11 (b), 6.60 (b), 4.80(s), 1.85 (b), 1.40 (b); ¹³C NMR (100 MHz, CDCl₃) δ (ppm) 186.21, 145.48, 127.90, 127.62, 125.72, 77.35, 77.01, 76.73, 40.35, 21.96; UV (λ max, nm, CH₂Cl₂) 250, 320 (w).
Grafting of PEG onto BCBO-PSt (III-4)

Polymer III-4 (150 mg) and poly(ethylene glycol) methyl ether (3 g) were dissolved in dichloromethane in an UV cell, and stirred at the ambient temperature to be UV irradiated (100 Mw mercury lamp, beam light around 320 nm) for 1-2 hours. The reaction mixture was then poured into water. The resulting mixture was centrifuged. The product was washed with water in a Soxhlet extractor overnight. The resulting beige polymer was then dried at 50 °C under vacuum. Yields were quantitative.

**IV-3a-550** (5 % BCBO-PSt + PEG-550): GPC $M_w = 9,955$, $M_n = 6,010$, $M_w/M_n = 1.66$; IR (KBr, cm$^{-1}$) 3026, 2924, 1720, 1601, 1493, 1452, 1109; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ (ppm) 7.10 (b), 6.55 (b), 3.67(s), 2.61, 2.54, 2.48 (3 s, 3H), 2.10(b), 1.85 (b), 1.44 (b); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 127.96, 127.65, 125.65, 118.37, 70.59, 40.33.

**IV-3b-550** (10 % BCBO-PSt + PEG-550): GPC $M_w = 4,025$, $M_n = 2,630$, $M_w/M_n = 1.53$; IR (KBr, cm$^{-1}$) 2922, 1720, 1601, 1493, 1452, 1102; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ (ppm) 7.08 (b), 6.59 (b), 3.67(s), 3.40(s), 2.60, 2.53, 2.48 (3 s, 3H),
2.28 (b), 1.83 (b), 1.43 (b); \(^1\)\(^3\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 127.96, 127.65, 125.49, 118.42, 71.94, 70.59, 59.08, 40.28.

**IV-3a-2000** (5 % BCBO-PSt + PEG-2000): IR (KBr, cm\(^{-1}\)) 2922, 1720, 1601, 1493, 1452, 1102.

**IV-3b-2000** (10 % BCBO-PSt + PEG-2000): IR (KBr, cm\(^{-1}\)) 2922, 1720, 1601, 1493, 1452, 1102.

**Surface Modification of Polyethylene Film**

The process was shown in Scheme IV.7. The BCBO polyoctadecene III-7 was first spin coated from its chloroform solution on a 0.22 mm thick polyethylene (PE) film, followed by spraying with hydroxy-containing PEG [CH\(_3\)(OCH\(_2\)CH\(_2\))\(_n\)OH, Mw=550] and UV irradiated for about 1 min (spot cure) at ambient temperature. An excess of PEG was washed away with methanol. The film was dried under vacuum in order to be investigated by IR-ATR, XPS, and UV-Vis spectroscopy.

The dye-stained test was performed on the grafted surface as shown in Scheme IV.7. The hydrophilic PEG was coated on BCBO-PE surface, and then UV irradiated through a photo mask. After an excess of PEG was washed away, the PE film surface was sprayed with 0.5 wt % aqueous solution of 3,3'-diethylthiadicarbocyanine iodide and then cleaned with water.
UV Curing of Polyimide III-10

Thin films were obtained by casting the polymer solution on quartz plates. After drying at ambient temperature for about 36 hours, the films were exposed on one side to UV spot light.

Photopatterning of Polyimide III-10

The experiments were carried out at the Institute for Microstructural Sciences in Ottawa of the National Research Council. Sample solutions (0.025 g/mL) prepared for photolithography were spin coated at 4000 rpm on silicon wafers. These films were then exposed to UV light on a KarlSuss MJB3 Mask Aligner. The exposed samples were then developed by soaking in chloroform for 30 seconds. Micrographs were taken on an Olympus optical microscope. The scanning electron micrographs of the polyimide patterns were taken using a JEOL JSM-6400 Scanning Microscope. The surface depth profiles were determined with a Dektek ST Surface Profiler (Veeco Sloan Technology, Inc.).
IV.5. References


7. J. Li; T. Yoshizawa; M. Ikuta; M. Ozawa; K. Nakahara; T. Hasegawa; K. Kitazawa; M. Hayashi; K. Kinbara; M. Nohara; K. Saigo, *Chem. Lett.*, 1997, 1037.


SUMMARY

Benzocyclobutenone (BCBO) has been evaluated as a ketene precursor in a novel curing chemistry. BCBO has been chemically functionalized, such as 5-aminobenzocyclobutenone (III-2), for incorporation into a variety of commercially and experimentally available polymers. Benzocyclobutenone has been incorporated into a wide spectrum of vinyl polymers as a pendent group through copolymerization of vinyl monomers or through grafting onto anhydride-containing and carboxylic acid-containing polymers via imidization transformation and amide coupling, respectively. The result is a series of polymers which share a common functionality (latent reactive vinyl ketene) yet differ drastically in their polymeric structure (intrinsic properties), permitting further manipulation via grafting, branching, and crosslinking.

The applications of BCBO-containing polymers have been exploited, based on the reactions with [60]fullerene (C<sub>60</sub>) and alcohols. Quantitative incorporation of C<sub>60</sub> into vinyl polymers (e.g., polystyrene and polyethylene) has been achieved by reaction of the precursor BCBO polymers with C<sub>60</sub> in 1,2-dichlorobenzene. The amount of C<sub>60</sub> in the polymer is dictated by the BCBO content in the precursor polymer which can easily be controlled through copolymerization or grafting.

Bulk modifications of polystyrene and surface modification of polyethylene films have been successfully demonstrated via the photochemical reaction of BCBO with alcohols. The modified BCBO polystyrene is reacted with poly(ethylene glycol) methyl ether (PEG-OH) to form a grafted polymer with hydrophilic aliphatic chain. The surface
of polyethylene film can be made hydrophilic by coating with a compatible BCBO polymer and subsequent photo-grafting with PEG-OH.

Photocurable polymethacrylates and polyimides containing the BCBO and hydroxyl groups have been synthesized and are capable of undergoing a self crosslinking reaction upon UV irradiation either in solution or in the solid state. High-resolution photo-patterns on a silicon wafer are readily formed by a simplified photolithographic process involving spin coating, UV irradiation at ambient temperatures and wet etching.
CONTRIBUTION TO KNOWLEDGE

1. This work demonstrates that the thermal cycloaddition reaction of BCBO with a dienophile and the photochemical reaction of BCBO with an alcohol can be applied to the polymer systems.

2. This work demonstrates that the BCBO group can be incorporated into a variety of commercially and experimentally available, both addition- and condensation-type polymers by direct polymerization and post polymerization.

3. This work demonstrates that the BCBO polymers can undergo the grafting and crosslinking reactions with a wide range of alcohols, affording the polymers with different properties in bulk or on the surface.

4. This work demonstrates that the polymers containing the BCBO and hydroxy groups can be cured by light at ambient temperatures, which can be used to generate the high-resolution patterns on substrates by photolithography without a baking step.

5. This work demonstrates that the BCBO polymers have potential applications as new photocurable materials in industry.