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REACTIVITY OF VEGETABLE OIL MACROMONOMERS IN THIOL-ENE, CATIONIC, AND EMULSION POLYMERIZATIONS

Micah Stephen Black
University of Southern Mississippi

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The University of Southern Mississippi

REACTIVITY OF VEGETABLE OIL MACROMONOMERS IN THIOL-ENE,
CATIONIC, AND EMULSION POLYMERIZATIONS

by

Micah Stephen Black

A Dissertation
Submitted to the Graduate Studies Office
of The University of Southern Mississippi
in Partial Fulfillment of the Requirements
for the Degree of Doctor of Philosophy

May 2007
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ABSTRACT

REACTIVITY OF VEGETABLE OIL MACROMONOMERS IN THIOL-ENE, CATIONIC, AND EMULSION POLYMERIZATIONS

by Micah Stephen Black

May 2007

Vegetable oils were, and continue, to be a mainstay in unsaturated polyester ("alkyd") technology. Our endeavor is to use vegetable oil-based polymers in environmentally-friendly coatings. The role of vegetable oil cis-unsaturation has not been fully explored in polymers. To that end, vegetable oil macromonomers (VOMMs) in three different systems were investigated to determine the involvement of cis-unsaturation in chain transfer, auto-oxidation, and copolymerization reactions. VOMMs were incorporated into UV curable thiol-ene coatings, UV cationic coatings, and acrylic solution copolymers and fundamental studies were conducted to determine how and to what extent cis-unsaturation contributes to film performance properties.

In thiol-ene UV curable coatings, cis-unsaturation was involved in the initial curing reaction and to lesser degrees, in postcure crosslinking. Its behavior was determined to be dependent on the ene component. Thiol-ene photopolymerization yielded homogeneous networks but formulations containing VOMMs exhibited greater heterogeneity due to non-uniformity in the VOMM chemical structures, and the concurrent reactions occurring during thiol-ene photopolymerization and "dark cure".

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Partially epoxidized soybean oil was synthesized to contain varying levels of residual cis-unsaturation. Cationic photopolymerization of partially epoxidized soybean oil yielded lightly crosslinked films, but the influence of free radical decomposition byproducts has not been fully investigated. The low involvement of the cis-unsaturation in photopolymerization was attributed to its low reactivity and/or radical combination with antioxidants and molecular oxygen dissolved in the films.

When used in emulsion polymerization, VOMMs lower the minimum filming temperature during coalescence and increase the T_g after application via auto-oxidation. Free radical polymerization of VOMMs is accompanied by chain transfer reactions between polymer radicals and VOMMs that reduces molecular weight and the auto-oxidation potential of the film. Retardation in polymerization rate correlated directly with increase in amount of unsaturation and conjugated unsaturation. Vegetable oils containing significant amounts of fatty acids with bisallylic hydrogen atoms were found to be more reactive towards chain transfer than fatty acids containing monoallylic hydrogen atoms. Model polymers were produced by functionalizing methacrylic copolymers through a mild reaction pathway in the absence of radicals. Copolymers with large quantities of bisallylic hydrogen atoms showed increased auto-oxidation reactivity as evidenced by greater consumption of cis-unsaturation and higher gel fractions.
ACKNOWLEDGEMENTS

I would like to start my acknowledgements by first giving sincere thanks to Dr. Shelby F. Thames, who has established a tradition for scientific and professional excellence in polymer science. I also thank my advisor, Dr. James Rawlins, and my committee members, Drs. Charles Hoyle, Douglas Wicks, William Jarrett, and James Evans for their support and direction of my research project. Each and every one of these gentlemen has helped me reach the goals that I set out to accomplish in the beginning of my graduate research.

I want to thank Drs. Douglas Wicks, Lon Mathias, and Judy Giordan for their leadership during my fellowship in the IGERT program. The teamwork exercises, discussions with start-up companies, and international experience will no doubt be of great benefit to me in my professional career. I also would like to acknowledge Dr. Robert Gilbert and his research associates at the Key Centre for Polymer Colloids, University of Sydney, AU, for allowing me to work with them in their laboratory and for giving me their full support and assistance.

I would like to thank my fellow researchers in the Thames-Rawlins research group. Jeremy Swanson, James Whittemore, David Dellatte, and many undergraduate researchers have helped me in various aspects of my research and I give each and every one thanks. I also thank Sharathkumar Mendon and Debbie Witherby for editing manuscripts, documents, and presentations that I have written and presented over the course of my PhD research. Finally I give thanks to my family who have supported me and have always been there to pick me up when I have fallen and have pushed me to excel in all my endeavors.
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LIST OF ABBREVIATIONS

% - percentage
$^{13}$C - carbon 13
$^1$H - proton
2-HEA - 2-hydroxyethyl acrylate
2-HEMA - 2-hydroxyethyl methacrylate
3-CPBA - 3-chloroperoxybenzoic acid
4-HBVE - 4-hydroxybutyl vinylether
4-MEHQ - 4-methoxyhydroquinone
AA - allyl alcohol
AIBN - 2,2'-azobis(2-methylpropionitrile)
APT - attached proton test
ASTM - american standard for testing materials
ATR - attenuated total reflectance
BA - butyl acrylate
CAM - castor acrylate monomer
CDCl$_3$ - deuterated chloroform
cm - centimeter
DABCO - 1,4-diazabicyclo[2.2.2]octane
DBTDL - dibutyltin dilaurate
DCC - dicyclohexylcarbodiimide
DCU - dicyclohexylurea
DiComp - diamond composite
DMA – dynamic mechanical analysis
E' – storage modulus
EB – electron beam
ESO – epoxidized soybean oil
FA – fatty acid
ft – feet
FTIR – fourier transform infrared
g – grams
GPC – gel permeation chromatography
HDDA – hexanediol diacrylate
HPLC – high performance liquid chromatography
HQ – hydroquinone
Hz – hertz
in – inch
IPDI – isophorone diisocyanate
IR – infrared
kcal – kilocalories
k_{CT} – chain transfer constant
k_p – propagation constant
L – linoleic
l – liter
lb – pound
Ln – linolenic
M - molar

$M_c$ – molecular weight between crosslinks

MEK – methyl ethyl ketone

MFT – minimum film formation temperature

mg – milligram

MG – monoglyceride

min – minute

ml – milliliter

mm – millimeter

MMA – methyl methacrylate

mmol – millimole

$M_n$ – number average molecular weight

mol – moles

$M_p$ – molecular weight at peak maximum

MSO – maleinized soybean oil

$M_w$ – weight average molecular weight

MWD – molecular weight distribution

nm – nanometer

NMR – nuclear magnetic resonance

O – oleic

P – palmitic, poise

PDI – polydispersity index

PEG1000 – poly(ethylene glycol) with a molecular weight = 1000 g/mol
phr – parts per hundred resin
PMMA – poly(methyl methacrylate)
ppm – parts per million
PTZ – phenothiazine
R – gas constant
RI – refractive index
rpm – revolutions per minute
RTIR – real time infrared
S – stearic
SAM – soybean acrylate monomer
SBO – soybean oil
SiComp – silicon composite
Soy-AA – soybean amide acrylate
T – temperature
tan – tangent
T_g – glass transition temperature
THF – tetrahydrofuran
UCAM – urethane modified castor acrylate monomer
UV – ultraviolet
UV-VIS – ultraviolet-visible
V_c – crosslink density
VM – vinyl monomer
VOC(s) – volatile organic compound(s)
VOMM(s) – vegetable oil macromonomer(s)

w – weight fraction

wt – weight

$X_n$ – number average degree of polymerization
CHAPTER I
INTRODUCTION

Vegetable oil macromonomers (VOMMs) are reactive monomer derivatives using vegetable oils as a feedstock and for the following discussion are most often acrylate functional. VOMMs are usually designed for use in emulsion polymerization and have recently been formulated into ultraviolet (UV) curable coatings to produce high performance coating materials. The rationale for utilizing vegetable oils and other renewable natural products as building blocks in polymeric applications is more critical now than it has ever been. Rising petroleum costs and concerns over long-term crude oil stability have most noticeably impacted the fuel industry but has also directly impacted the petrochemical industry. This phenomenon has caused a paradigm shift, with consumers and manufacturers focusing increased attention to sustainable energy and feedstock sources. In addition to commercial drive, the federal government has aggressively funded research towards "new carbon" technology development and biomass utilization.

Vegetable oils are in a pivotal position, playing a significant role in the crossover from a petroleum-dependent past to a petroleum-independent future. The largest use of vegetable oils is in the food industry, while non-food applications include biodiesel, composites, lubricants, foams, coatings, surfactants, and oleochemicals.\textsuperscript{1-7} Biodiesel has received a significant amount of media attention recently as an alternative and supplement to diesel/gasoline. Figure 1-1 summarizes the number of biodiesel patents issued since 1994.\textsuperscript{8} The
technological development and use of vegetable oils has also grown in other applications, although not quite as explosively as biodiesel.

![Biodiesel patent histogram.]

Our lab as well as others worldwide has been actively performing research to better utilize vegetable oil derivatives and technology as a renewable feedstock for coatings and coating-related technologies. The coatings market is a $30 billion business annually with 2005 sales approaching $20 billion in the U.S. Table 1-1 summarizes a breakdown of the quantity and value of coatings sold in the U.S. over the course of the last six years. The trend in architectural coatings has been of steady sales increases, normally tracking with the growth in the national gross domestic product (GDP).
Table 1-1. Summary of Estimated United States Coatings’ Market\textsuperscript{10}

<table>
<thead>
<tr>
<th>Year</th>
<th>Total</th>
<th>Architectural</th>
<th>OEM</th>
<th>Special-purpose</th>
<th>Miscellaneous</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Quantity</td>
<td>Value</td>
<td>Quantity</td>
<td>Value</td>
<td>Quantity</td>
</tr>
<tr>
<td>2005</td>
<td>1,530</td>
<td>19,868</td>
<td>795</td>
<td>8,946</td>
<td>402</td>
</tr>
<tr>
<td>2004</td>
<td>1,534</td>
<td>19,233</td>
<td>804</td>
<td>8,623</td>
<td>404</td>
</tr>
<tr>
<td>2003</td>
<td>1,474</td>
<td>18,092</td>
<td>762</td>
<td>8,006</td>
<td>399</td>
</tr>
<tr>
<td>2002</td>
<td>1,434</td>
<td>17,466</td>
<td>710</td>
<td>7,510</td>
<td>409</td>
</tr>
<tr>
<td>2001</td>
<td>1,393</td>
<td>17,275</td>
<td>667</td>
<td>7,038</td>
<td>407</td>
</tr>
<tr>
<td>2000</td>
<td>1,467</td>
<td>17,725</td>
<td>651</td>
<td>6,461</td>
<td>453</td>
</tr>
</tbody>
</table>

Note: Quantity in millions of gallons; value in millions of dollars.

Table 1-1 illustrates the tremendous research opportunities that exist in coatings. A critical driver for coatings research over the past fifteen years has been the requirement to reduce/eliminate volatile organic compounds (VOCs) in coatings of all types. VOCs have traditionally been a major component of coatings, used to reduce the application viscosities in solvent-based coatings and act as coalescing aids in waterborne coatings. Next to automobile emissions/pollutants, coatings are the second largest emitter of man-made VOCs.\textsuperscript{11}

VOCs are environmentally harmful because they react with nitrogen oxides to form ground level ozone (smog), which results in respiratory problems, especially in large cities. The Clean Air Act Amendments (CAAAs) enacted in 1990 regulate the VOC levels in coatings by imposing stringent emission requirements on coatings manufacturers and promoting the development of environmentally-responsible materials.\textsuperscript{12} Since the enactment of the CAAAs, the Environmental Protection Agency (EPA) has progressively lowered the...
acceptable amounts of VOCs in coatings, compelling coatings manufacturers to consistently reformulate their coatings to ensure VOC compliance.

Ideally, using VOMMs as comonomers in emulsion polymerization enables film coalescence without externally added cosolvents through a plasticization mechanism, thereby eliminating the need for VOCs. The technology is also attractive because vegetable oils provide the opportunity for ambient crosslinking via auto-oxidation after coating application. As the data herein will validate, VOMMs enhance flexibility without sacrificing other important film properties such as impact and solvent resistance when they are used as prepolymers in UV curable coatings. Furthermore, the vegetable oil unsaturation also contributes to post-cure crosslinking. There are already many commercial coating applications for vegetable oils including alkyds, oil-modified polyurethane dispersions, epoxy esters, emulsions, and UV curable coatings. Only alkyds, emulsions, and UV curable materials, along with a discussion of vegetable oils and auto-oxidation, will be considered in this chapter.

**Vegetable Oils**

Vegetable oils are triglyceride esters of mixed fatty acids and their general structure is shown in Figure 1-2. These compounds vary in molecular weight, unsaturation content, and conjugation depending upon plant type, soil conditions, humidity, temperature, method of extraction, and process control. Table 1-2 summarizes common oils along with their major fatty acid components and percentages.
Figure 1-2. Generic vegetable oil structure with unsaturated fatty acids.

Table 1-2. Oils and Fatty Acid Contents

<table>
<thead>
<tr>
<th>Oil</th>
<th>Saturated</th>
<th>Oleic</th>
<th>Linoleic</th>
<th>Linolenic</th>
<th>α-Eleostearic</th>
</tr>
</thead>
<tbody>
<tr>
<td>Soybean</td>
<td>15</td>
<td>22</td>
<td>55</td>
<td>8</td>
<td>-</td>
</tr>
<tr>
<td>Sunflower</td>
<td>12</td>
<td>15</td>
<td>73</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Linseed</td>
<td>9</td>
<td>17</td>
<td>14</td>
<td>60</td>
<td>-</td>
</tr>
<tr>
<td>Tung</td>
<td>5</td>
<td>11</td>
<td>15</td>
<td>-</td>
<td>69</td>
</tr>
<tr>
<td>Safflower</td>
<td>6</td>
<td>16</td>
<td>78</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Note: Saturated oils also contain very small fractions of other unsaturated fatty acids.

Of importance to note is the fact that the fatty acid composition in the oils presented in the table above are approximate values. Soybean oil, for example, ranges from 11-20% in saturated fatty acids (trace–0.5 myristic and lower, 7-11 palmitic, 2-6 stearic, and 0.3-3 C\textsubscript{20} and higher) and 82-90% in unsaturated fatty acids (trace-1 C\textsubscript{16} and lower, 15-33 oleic, 43-56 linoleic, 5-11 linolenic). All other vegetable oils will also contain fatty acid ranges. Also, fatty acids are unevenly distributed in the triglyceride molecules. Table 1-3 lists the fatty acid composition for common unsaturated vegetable oils as reported by List and coworkers\textsuperscript{14} using a high-pressure liquid chromatography (HPLC)-flame ionization detection method. The fatty acid constituent break-down allows for distribution determination for the quantity of double bonds per triglyceride. Figure 1-3

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reveals that the largest weight fraction (28%) of soybean oil triglycerides contains 4 double bonds with lower fractions containing triglycerides with quantities greater than and less than 4.\textsuperscript{14}

Table 1-3. Triglyceride Composition of Common Vegetable Oils by HPLC\textsuperscript{14}

<table>
<thead>
<tr>
<th>Triglyceride</th>
<th>Canola</th>
<th>Peanut</th>
<th>Corn</th>
<th>Cottonseed</th>
<th>Soybean</th>
<th>Sunflower</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ln-Ln-Ln</td>
<td>0.1</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>Ln-Ln-L</td>
<td>0.3</td>
<td>0.0</td>
<td>0.0</td>
<td>0.1</td>
<td>0.7</td>
<td>0.0</td>
</tr>
<tr>
<td>Ln-Ln-L</td>
<td>1.2</td>
<td>0.1</td>
<td>0.6</td>
<td>0.1</td>
<td>6.3</td>
<td>0.0</td>
</tr>
<tr>
<td>Ln-Ln-O</td>
<td>1.3</td>
<td>0.0</td>
<td>0.0</td>
<td>0.1</td>
<td>0.2</td>
<td>0.0</td>
</tr>
<tr>
<td>Ln-Ln-P</td>
<td>0.1</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.1</td>
<td>0.0</td>
</tr>
<tr>
<td>L-L-L</td>
<td>2.7</td>
<td>1.9</td>
<td>23.4</td>
<td>18.8</td>
<td>17.2</td>
<td>32.4</td>
</tr>
<tr>
<td>Ln-L-O</td>
<td>6.4</td>
<td>0.2</td>
<td>0.9</td>
<td>1.2</td>
<td>5.0</td>
<td>1.1</td>
</tr>
<tr>
<td>Ln-L-P</td>
<td>1.0</td>
<td>0.1</td>
<td>0.4</td>
<td>0.8</td>
<td>2.5</td>
<td>0.2</td>
</tr>
<tr>
<td>L-L-O</td>
<td>9.0</td>
<td>13.0</td>
<td>23.4</td>
<td>2.6</td>
<td>17.9</td>
<td>27.9</td>
</tr>
<tr>
<td>Ln-O-O</td>
<td>9.6</td>
<td>0.4</td>
<td>0.5</td>
<td>0.5</td>
<td>1.3</td>
<td>0.4</td>
</tr>
<tr>
<td>L-L-P</td>
<td>3.0</td>
<td>3.8</td>
<td>15.7</td>
<td>27.8</td>
<td>12.9</td>
<td>10.7</td>
</tr>
<tr>
<td>Ln-O-P</td>
<td>1.8</td>
<td>0.2</td>
<td>0.4</td>
<td>1.6</td>
<td>1.1</td>
<td>0.3</td>
</tr>
<tr>
<td>Ln-P-P</td>
<td>0.1</td>
<td>0.6</td>
<td>0.3</td>
<td>0.3</td>
<td>0.1</td>
<td>0.2</td>
</tr>
<tr>
<td>L-O-O</td>
<td>21.7</td>
<td>21.1</td>
<td>10.9</td>
<td>3.7</td>
<td>9.5</td>
<td>6.7</td>
</tr>
<tr>
<td>L-L-S</td>
<td>1.0</td>
<td>0.9</td>
<td>2.1</td>
<td>1.8</td>
<td>3.2</td>
<td>7.4</td>
</tr>
<tr>
<td>L-O-P</td>
<td>5.8</td>
<td>11.8</td>
<td>10.4</td>
<td>12.9</td>
<td>9.2</td>
<td>4.8</td>
</tr>
<tr>
<td>P-L-P</td>
<td>1.1</td>
<td>2.8</td>
<td>1.7</td>
<td>10.8</td>
<td>1.6</td>
<td>0.7</td>
</tr>
<tr>
<td>O-O-O</td>
<td>23.6</td>
<td>15.7</td>
<td>3.3</td>
<td>1.0</td>
<td>3.1</td>
<td>1.7</td>
</tr>
<tr>
<td>L-O-S</td>
<td>1.3</td>
<td>2.4</td>
<td>1.5</td>
<td>0.8</td>
<td>2.7</td>
<td>2.2</td>
</tr>
<tr>
<td>P-O-O</td>
<td>4.8</td>
<td>8.7</td>
<td>2.4</td>
<td>0.0</td>
<td>2.3</td>
<td>0.6</td>
</tr>
<tr>
<td>S-L-P</td>
<td>1.1</td>
<td>4.8</td>
<td>0.6</td>
<td>1.4</td>
<td>0.9</td>
<td>0.7</td>
</tr>
<tr>
<td>P-O-P</td>
<td>0.3</td>
<td>1.8</td>
<td>0.6</td>
<td>1.3</td>
<td>0.6</td>
<td>0.8</td>
</tr>
<tr>
<td>P-P-P</td>
<td>0.3</td>
<td>1.0</td>
<td>0.2</td>
<td>1.9</td>
<td>0.1</td>
<td>0.1</td>
</tr>
<tr>
<td>S-O-O</td>
<td>1.4</td>
<td>3.0</td>
<td>0.4</td>
<td>0.1</td>
<td>0.7</td>
<td>0.4</td>
</tr>
<tr>
<td>S-L-S</td>
<td>0.3</td>
<td>1.6</td>
<td>0.2</td>
<td>0.2</td>
<td>0.2</td>
<td>0.3</td>
</tr>
<tr>
<td>S-O-P</td>
<td>0.4</td>
<td>1.4</td>
<td>0.2</td>
<td>0.2</td>
<td>0.3</td>
<td>0.3</td>
</tr>
<tr>
<td>P-P-S</td>
<td>0.1</td>
<td>2.0</td>
<td>0.1</td>
<td>0.1</td>
<td>0.1</td>
<td>0.1</td>
</tr>
<tr>
<td>S-O-S</td>
<td>0.1</td>
<td>0.7</td>
<td>0.1</td>
<td>0.0</td>
<td>0.0</td>
<td>0.1</td>
</tr>
<tr>
<td>P-S-S</td>
<td>0.0</td>
<td>0.7</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.1</td>
</tr>
<tr>
<td>S-S-S</td>
<td>0.0</td>
<td>0.2</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
</tbody>
</table>

\textsuperscript{14}Ln = linolenic (C18, 3 double bonds), L = linoleic (C18, 2 double bonds), O = oleic (C18, 1 double bond), P = palmitic (C16, saturated), S = stearic (C18, saturated)
Number of double bonds per triglyceride

Other significant oils include castor oil and vernonia oil. Castor oil contains approximately 90% ricinoleic acid (Figure 1-4) and vernonia oil contains approximately 80% vernolic acid (Figure 1-5). The functional groups, hydroxyl and epoxide, present in these oils offer broader reaction options for functionalization, e.g., reaction with isocyanates, amines, carboxylic acids, and anhydrides, to name a few.

Figure 1-4. Ricinoleic acid structure.
Internal Unsaturation and Auto-Oxidative Polymerization

Vegetable oils are classified into 3 categories, namely, drying oils (harden to a tough, solid film upon exposure to air), semi-drying oils (partially harden when exposed to air), and non-drying oils (remain tacky even upon prolonged exposure to air). The drying ability of vegetable oils is quantified and dependent upon their specific iodine values. Iodine value is defined as the mass (in grams) of iodine that is absorbed via reaction with unsaturation by 100 g of vegetable oil. Drying oils such as tung, oiticica, linseed, and perilla have iodine values greater than 150 g/100 g of oil. Semi-drying oils such as soybean, sunflower, safflower, and tall oil have iodine values between 120-150 g/100 g of oil. Non-drying oils such as castor oil and coconut oil have iodine values of less than 120 g/100 g of oil.¹⁵

Drying oils form tack-free films via oxidative crosslinking. Auto-oxidative polymerization proceeds through two stages: primary and secondary oxidation. These two stages encompass six main steps which include:¹⁶

1. Induction period
2. Initiation
3. Hydroperoxide formation
4. Hydroperoxide decomposition
5. Crosslinking
6. Formation of low molecular weight byproduct

Vegetable oils contain natural antioxidants such as α and β-tocopherols, which inhibit oxidation through radical scavenging reactions. When the antioxidants are consumed, oxygen will abstract allylic hydrogen atoms creating resonance stabilized allylic radicals. Oxygen uptake and hydroperoxide (both cyclic and acyclic) formation are accompanied by an increase in the degree of double-bond conjugation. The resultant allylic radicals quickly react with oxygen to form peroxy radicals. Secondary oxidation occurs next, characterized by loss of unsaturation and C-C and C-O-C bond formation via peroxide decomposition leading to radical recombination and double bond addition reactions. Metal driers accelerate auto-oxidation by decreasing the activation energy for hydroperoxide decomposition via redox mechanisms. Cobalt and manganese salts function almost exclusively as primary driers in curing the coating surface, whereas zirconium and calcium salts serve as secondary driers promoting even drying throughout the bulk film. Not all of oxidation reactions lead to crosslinks however. β-scission reactions between alkoxy radicals and fatty acids form low molecular weight products such as alcohols, ketones, carboxylic acids, and aldehydes. The putrid smell associated with the later stages of vegetable oil oxidation has been ascribed to aldehyde formation. Primary and secondary oxidation is illustrated in Figures 1-6 and 1-7, respectively.
Coatings Applications for Vegetable Oils

Vegetable oils have a long history as binders for coatings, dating back to the 2nd century when the Greek physician Galen mixed oils with white lead, litharge, and umber. However, it was not until 1440 when the first varnishes were formulated with linseed oil that vegetable oils were used as protective coatings. Alkyds, or oil-modified polyesters, emerged in the late 1920s and are
still widely used today but have been replaced in many applications by other synthetic resins. Nevertheless, alkyds continue to be the subject of significant research and new product development, as revealed by the alkyd patent histogram shown in Figure 1-8.

![Figure 1-8. Alkyd patent histogram.](image)

Alkyds consist of vegetable oils/fatty acids, polyols, and polybasic acids, and are synthesized either through the fatty acid (FA) process or the monoglyceride (MG) process (Figure 1-9). The fatty acid process is more expensive because fatty acids have to be isolated from vegetable oils, and stainless steel or glass reactors must be used for esterification. However, this process offers great flexibility in altering the alkyd fatty acid composition to tailor performance properties. The monoglyceride process is less expensive, but the final alkyd always includes a mixture of fatty acids inherent to the vegetable oils used in the synthesis, and tuning the drying properties is therefore more difficult. Alkyds are versatile in performance, easy to modify, and are cost effective, but
they have limited hydrolytic stability and tend to yellow with time. Although 100% solids alkyds are commercially available, most alkyds are thinned with solvents to reduce their viscosity and inherently contain VOCs.

![Alkyd synthesis diagram](image)

R = fatty acid moieties

**Figure 1-9. Alkyd synthesis.**

Waterborne coatings employ water as the continuous phase, and encompass emulsions (latexes), water-soluble resins, and water-dispersible systems, with emulsions being the most widely used of the three. These coatings offer the advantages of environmental friendliness, low toxicity, reduced fire hazards, and ease of cleanup and application. Latex research has grown in importance since the mid-1930s to meet the U.S. demand for synthetic rubber during World War II, and rose dramatically in the 1960s when greater understanding of emulsion polymerization and reduction-to-practice fueled commercialization. Figure 1-10 shows the patent histogram for latexes, representing all latex applications, including coatings.
Emulsions are characterized as surfactant-stabilized polymer particles dispersed in water. Thermoplastic latexes (molecular weight 100,000 - 1,000,000 g/mol) rely on chain entanglement for physical properties and are the most widely used emulsion polymers.\textsuperscript{23} Thermosetting latexes are generally designed to contain lower molecular weight functionalized polymers, such as hydroxyl functional copolymers, and crosslinkers, such as hexamethoxymethylmelamine, that react after water evaporation to form tough coatings.

Monomers employed in emulsion polymerization are typically $\alpha,\beta$-unsaturated monofunctional compounds that are copolymerized in various ratios depending on the desired cost and performance properties, such as minimum filming temperature (MFT), hardness, and glass transition temperature ($T_g$). Table 1-4 lists commonly used monomers along with the $T_g$ values for the resultant homopolymers.\textsuperscript{24} The $T_g$ of random copolymers is approximated using
the Fox equation, where $W_{(n)}$ is the weight fraction of each monomer and $T_{g(n)}$ is the respective homopolymer $T_g$ as reported in Kelvin (Equation 1-1).  

\[ \frac{1}{T_g} = \frac{W_1}{T_{g1}} + \frac{W_2}{T_{g2}} + \ldots \]

**Table 1-4. Homopolymer $T_g$s of Common Latex Monomers**

<table>
<thead>
<tr>
<th>Monomer</th>
<th>Homopolymer $T_g$ ($^\circ$C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Butyl acrylate</td>
<td>-54</td>
</tr>
<tr>
<td>Vinyl acetate</td>
<td>32</td>
</tr>
<tr>
<td>Styrene</td>
<td>100</td>
</tr>
<tr>
<td>Methyl methacrylate</td>
<td>105</td>
</tr>
<tr>
<td>Methacrylic acid</td>
<td>225</td>
</tr>
</tbody>
</table>

**Equation 1-1. Fox equation.**

Emulsion polymers form films via coalescence of latex polymer particles. The polymer particles must have a low MFT to enable migration, diffusion, and entanglement of polymer chains between neighboring particles. Latexes used in architectural coatings are designed with $T_g$'s below ambient temperature (~10°C). The logic is as follows. If the $T_g$ is too low, the film will be tacky and pick up contaminants after application, while a higher than ambient $T_g$ will necessitate other mechanisms for film formation and sufficient polymer-polymer entanglement for film integrity. The traditional option has been to design polymer Tg's above ambient and then add coalescing solvents to achieve good film formation. These organic solvents temporarily reduce the MFT to provide good coalescence and physical entanglement. Subsequent to film formation, the
cosolvents evaporate, and the film regains the \( T_g \) dictated by its copolymer composition. The cosolvents that constitute the VOC content of waterborne coatings are often required at a level of 250g/L. VOMMs were designed to eliminate VOC emissions by temporarily solvating/plasticizing latex particles and individual polymer chains facilitating low/zero VOC latexes with good coalescence and chain entanglement characteristics. The fatty acid hydrocarbon tails reduce the \( T_g \) of the binder, thus reducing MFT. Stevens showed that increasing hydrocarbon sidechain length initially decreases the \( T_g \) to a point, due to plasticization, after which the \( T_g \) began to increase due to crystallization as shown in Table 1-5.\(^{26}\) A similar trend was observed in methacrylate homopolymers (Table 1-6).\(^{27}\) The side chains act similar to small molecular weight additives and in VOMM-based polymers, behave as non-fugitive plasticizers. It is critical to note that the crystallization behavior exhibited by longer side chains is less facile in copolymers, where the individual chains remain randomly isolated adjacent to the backbone.
Table 1-5. Glass Transition Temperatures of Vinyl Polymers\textsuperscript{26}

<table>
<thead>
<tr>
<th>Polymer</th>
<th>R</th>
<th>(T_g) (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polypropylene</td>
<td>(\text{CH}_3)</td>
<td>5</td>
</tr>
<tr>
<td>Poly(1-butene)</td>
<td>(\text{CH}_3\text{CH}_2)</td>
<td>-24</td>
</tr>
<tr>
<td>Poly(1-pentene)</td>
<td>(n\text{-C}_3\text{H}_7)</td>
<td>-40</td>
</tr>
<tr>
<td>Poly(1-hexene)</td>
<td>(n\text{-C}_4\text{H}_9)</td>
<td>-50</td>
</tr>
<tr>
<td>Poly(1-heptene)</td>
<td>(n\text{-C}<em>5\text{H}</em>{11})</td>
<td>-31</td>
</tr>
<tr>
<td>Poly(1-decene)</td>
<td>(n\text{-C}<em>6\text{H}</em>{17})</td>
<td>-41</td>
</tr>
<tr>
<td>Poly(1-dodecene)</td>
<td>(n\text{-C}<em>{10}\text{H}</em>{21})</td>
<td>-6</td>
</tr>
</tbody>
</table>

Table 1-6. Glass Transition Temperatures for Poly(\(n\)-Alkyl Methacrylates)\textsuperscript{27}

<table>
<thead>
<tr>
<th>Polymer</th>
<th>R</th>
<th>(T_g) (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Poly(methyl methacrylate)</td>
<td>(\text{CH}_3)</td>
<td>105</td>
</tr>
<tr>
<td>Poly(ethyl methacrylate)</td>
<td>(\text{CH}_3\text{CH}_2)</td>
<td>65</td>
</tr>
<tr>
<td>Poly((n)-propyl methacrylate)</td>
<td>(n\text{-C}_3\text{H}_7)</td>
<td>35</td>
</tr>
<tr>
<td>Poly((n)-butyl methacrylate)</td>
<td>(n\text{-C}_4\text{H}_9)</td>
<td>20</td>
</tr>
<tr>
<td>Poly((n)-hexyl methacrylate)</td>
<td>(n\text{-C}<em>6\text{H}</em>{13})</td>
<td>-5</td>
</tr>
<tr>
<td>Poly((n)-octyl methacrylate)</td>
<td>(n\text{-C}<em>6\text{H}</em>{17})</td>
<td>-20</td>
</tr>
<tr>
<td>Poly((n)-dodecyl methacrylate)</td>
<td>(n\text{-C}<em>{12}\text{H}</em>{25})</td>
<td>-65</td>
</tr>
</tbody>
</table>

In addition to alkyd and emulsion coatings, vegetable oils have also found application in UV curable materials. Epoxidized soybean oil has been used as the prepolymer component in cationic photopolymerization systems. Ultraviolet (UV) and electron beam (EB) curable materials fall under the class of radiation curable systems. UV coatings are more widely used than EB systems and will be the focus of this discussion. These materials had their beginning in coating
flat wood products but now are extensively used in applications such as electronics, fiber optics, compact discs, and high-gloss magazine covers. The patent histogram for UV curable materials is shown in Figure 1-11.

![Figure 1-11. UV curable patent histogram.](image)

The sale and utilization of UV curable materials has grown steadily since the 1970s. Typical UV curable technology is 100% solids and capable of almost instantaneous curing. The rapid transformation from liquid to solid films under ambient conditions permit productivity advantages over alternative technologies such as increased line speed, reduced energy consumption, and lower space requirements. Currently, UV curable coatings can be processed at rates up to 1000 ft/min.

Commercial UV curable coatings employ either free-radical or cationic chain-growth polymerizations, depending on monomer and photoinitiator choice. A less utilized but exciting technology are thiol-ene based materials, which polymerize via a step-growth mechanism that almost completely eliminates
oxygen inhibition. Often the offensive odor resulting from the presence of small amounts of low molecular weight thio impurities have hindered their commercial development. Thiol-ene systems are the focus of Chapter 4 and will be discussed in greater detail.

UV curable coatings consist of photoinitiators, reactive diluents, prepolymer (oligomers), pigments/additives, and a UV light source. Free-radical photoinitiators generate radicals through either a unimolecular (Type I) or bimolecular (Type II) process. Type I initiators, such as Darocur® 1173, are alpha-cleavage benzoin alkyl ethers (Figure 1-12). Type II initiators are benzophenone systems and produce radicals by either sensitizing a co-initiator (Irgacure® 500) or by abstracting hydrogen atoms from a donor amine (Figure 1-12).

Cationic photoinitiators will be discussed in greater detail in Chapter 5. Common cationic photoinitiators include sulfonium (such as UVI® 6974) and iodonium salts that form superacids when irradiated with UV light (Figure 1-13).
Reactive diluents are low molecular weight mono- and/or multifunctional materials used to adjust the viscosity of UV curable coatings and copolymerize with the prepolymer upon UV irradiation. Common reactive diluents include (meth)acrylates, styrene, vinyl ethers, and cycloaliphatic epoxides (Table 1-7). Crosslink density and cure rate increases with the degree of functionality. However, as functionality increases, the onset of vitrification (gelation) occurs at lower conversions and leads to incomplete functional group conversion. Therefore, a balance must be engineered between crosslink density, cure rate, and conversion.
### Table 1-7. Reactive Diluents

<table>
<thead>
<tr>
<th>Name</th>
<th>Functionality</th>
<th>MW(g/mol)</th>
<th>Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Styrene</td>
<td>1</td>
<td>104</td>
<td><img src="structure1.png" alt="Structure" /></td>
</tr>
<tr>
<td>Methyl acrylate</td>
<td>1</td>
<td>86</td>
<td><img src="structure2.png" alt="Structure" /></td>
</tr>
<tr>
<td>1,6-Hexanediol diacrylate</td>
<td>2</td>
<td>226</td>
<td><img src="structure3.png" alt="Structure" /></td>
</tr>
<tr>
<td>Trimethylolpropane triacrylate</td>
<td>3</td>
<td>282</td>
<td><img src="structure4.png" alt="Structure" /></td>
</tr>
<tr>
<td>Pentaerytritol tetraacrylate</td>
<td>4</td>
<td>352</td>
<td><img src="structure5.png" alt="Structure" /></td>
</tr>
<tr>
<td>UVR-6105</td>
<td>2</td>
<td>252</td>
<td><img src="structure6.png" alt="Structure" /></td>
</tr>
</tbody>
</table>

Prepolymers (Table 1-8) are the primary film formers in UV curable coatings and often dictate the coating’s final properties. They range in molecular weight from several hundred to several thousand atomic mass units and are generally (meth)acrylate end-terminated epoxies, polyethers, polyesters, and polyurethanes for free-radical polymerizations and diglycidyl ether of bisphenol-A (DGEBA) resins and derivatives for cationic polymerizations. Epoxidized seed oils such as epoxidized soybean and epoxidized linseed oils have also been used as prepolymerms for cationic polymerizations.32

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Table 1-8. UV Curable Prepolymers

<table>
<thead>
<tr>
<th>Name</th>
<th>General Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acrylated urethane</td>
<td><img src="image" alt="Acrylated urethane structure" /></td>
</tr>
<tr>
<td>Acrylated epoxide</td>
<td><img src="image" alt="Acrylated epoxide structure" /></td>
</tr>
<tr>
<td>Acrylated polyester</td>
<td><img src="image" alt="Acrylated polyester structure" /></td>
</tr>
<tr>
<td>Acrylated polyether</td>
<td><img src="image" alt="Acrylated polyether structure" /></td>
</tr>
<tr>
<td>DGEBA</td>
<td><img src="image" alt="DGEBA structure" /></td>
</tr>
<tr>
<td>Epoxidized oil</td>
<td><img src="image" alt="Epoxidized oil structure" /></td>
</tr>
</tbody>
</table>

Pigments and additives are added in smaller quantities than oligomers and reactive diluents and present challenges in formulation of UV curable coatings because they are also capable of absorbing UV light. This is especially true if formulating with a UV stabilizer or with a pigment such as titanium dioxide, which absorbs all wavelengths of UV light below 400 nm.33 Competitive.
absorption of photons leads to a reduction in the number of radicals/cations available to initiate polymerization, and limits the extent of cure. Several solutions have been suggested for this problem, the most practical being a judicious choice of photoinitiator and light source. The photoinitiator’s absorption profile must sufficiently overlap with the light source’s emission bands and lie outside the absorption profile of the pigment and additive. For TiO₂ pigmented coatings, a photoinitiator which absorbs at longer wavelengths (in the visible spectrum) is generally used.

Light sources employed in UV curable coatings include mercury vapor lamps (low, medium, and high pressure), pulsed xenon lamps, doped mercury lamps, electrodeless lamps, lasers, and light emitting diodes. The sources vary in emission wavelengths, emission intensity, power consumption, and bulb cost. Medium pressure mercury lamps are the most widely used light source, as they are relatively inexpensive, less hazardous than other bulb types, and have a wide emission spectrum. These lamps emit both high energy light (254 nm) to cure the coating surface and low energy light (366 nm) that deeply penetrate and cures the bulk of the coating.

In the last decade or so, vegetable oils, a sustainable feedstock, have been used to produce low cost, environmentally-friendly coatings with excellent physical properties. For example, WorléeSol E 150W (from Worlée-Chemie GmbH) is a commercially available medium oil polyurethane-alkyd emulsion containing approximately 44% vegetable oil. A semi-gloss coating formulated with WorléeSol E 150W had a 4-week scrub value of 383, methyl ethyl ketone
(MEK) resistance of 9 double rubs, and 5B dry adhesion. Coatings formed by cationically curing vernonia oil exhibited pencil hardness of 4B, 5B dry adhesion, and >160 in-lb direct impact resistance. Thiol-ene UV curable coatings containing VOMMs (>40% oil) produced in our lab exhibited MEK resistance of 300+ double rubs, 5B dry adhesion, 4H pencil hardness, 160 in-lb of direct impact, and 28% elongation for flexibility.

In addition to producing thiol-ene UV curable coatings with superior physical properties, we also gained greater understanding of auto-oxidation and chain-transfer reactions in vegetable oil based polymers. In particular, we know how and to what extent unsaturation is involved in postcure reactions in thiol-ene and cationic UV curable materials. We also have a better understanding of the chain transfer reactions that occur when (meth)acrylate monomers are polymerized in the presence of vegetable oils and its derivatives. With this knowledge, one can more accurately engineer emulsions based on VOMM structure/property relationships.
References:

8) Scifinder Scholar™ 2006.


CHAPTER II
RESEARCH PREVIEW

As stated in the Introduction, a consistent research goal throughout is to utilize biobased derivatives in coatings that provide polymer chain plasticization before film formation while harnessing the advantages of air drying via autooxidation of the vegetable oil unsaturation. Therefore, it is critical to understand and quantify the fate of vegetable oil macromonomer (VOMM) internal unsaturation, since all the fundamental studies relate to reactions involve the vegetable oil double bond in some way, shape, or form. The vegetable oil double bond has been identified as a chain transfer site; thus formulations are designed with a predetermined amount of unsaturation to participate in film building reactions. The amount and type of unsaturation is an important consideration for synthetic preparations and in designing high performance coatings, whether they are alkyds, waterborne, or UV curables.

Chapter 3 summarizes the experimental reagents used in VOMM synthesis, preparation, and formulation of coatings in combination with a brief description of the methods used throughout the research. VOMM structures were characterized using a variety of spectroscopic and chromatographic techniques, while coatings were analyzed using several postcure test methods to determine the nature and extent of crosslinking in each system. The reaction kinetics of photopolymerization, auto-oxidation, and chain transfer reactions were determined using infrared spectroscopy.
Chapter 4 discusses thiol-ene photopolymerization, a special form of free-radical polymerization characterized by step-growth addition that is uninhibited by molecular oxygen. Detailed descriptions are given for the synthesis of two types of VOMM prepolymers, namely Soybean oil based VOMMs and Castor oil based VOMMs. Their idealized acrylate functional VOMM structures are shown in Figure 2-1. The VOMMs were blended with trifunctional thiols and an α-cleavage photoinitiator to produce UV curable coatings. While Soy-VOMMs proved unusable as prepolymers in the thiol-ene coatings, Castor-VOMMs produced high gloss coatings with excellent physical properties. The polymerization rates of acrylate, allyl ether, and vinyl ether functional Castor-VOMMs were compared.

![Soy-VOMM and Castor-VOMM structures](image)

**Figure 2-1. Acrylate functional Soy and Castor-VOMM structures.**

A fundamental study was conducted to determine the extent and nature of postcure reactions in thiol-ene photopolymerizations. Fourier transform infrared (FTIR) spectroscopy, gel content, dynamic mechanical analysis (DMA), and postcure ASTM tests were conducted on films immediately after cure and after 1 week of postcure. The results indicate that internal unsaturation is involved in
initial curing, with the extent of reaction dependent on the ene functionality. It also makes a small contribution to continued crosslinking. Vinyl ether, allyl ether, and acrylate functional groups show continued reaction with thiol functional groups with time ("dark cure"), resulting in enhanced film properties.

Ideal thiol-ene networks were investigated as part of a co-project with fellow graduate student, Jeremy Swanson. Ideal networks formed very homogeneous crosslinked networks and were prepared from low molecular weight multifunctional vinyl ethers, acrylates, and thiols. These networks were compared to networks formed via thiol-ene polymerization of Castor-VOMMs to determine the relative degree of heterogeneity existing in these more complex systems (Figure 2-2).

Figure 2-2. Thiol-ene crosslinked networks.

Chapter 5 focuses on the role of unsaturation in the cationic photopolymerization of epoxidized soybean oil. There is much literature
discussing the use of fully epoxidized soybean oil, but very little research has been performed with partially epoxidized soybean oil. Since cationic photoinitiators generate both cations and radicals upon activation, it is of interest to determine the contribution of residual unsaturation to free-radical reactions. To that end, soybean oil was epoxidized partially and fully to form products containing various ratios of epoxy groups to unsaturation. FTIR spectroscopy was used to monitor functional group conversion, particularly, epoxy and cis-unsaturation consumption.

Chapter 6 details chain transfer reactions of common monomers polymerized in the presence of vegetable oils and their derivatives. Chain transfer reactions have the potential to reduce the polymer molecular weight and/or reduce/eliminate the auto-oxidative capability available after application. Several methods, including FTIR, gel permeation chromatography (GPC), and nuclear magnetic resonance (NMR) spectroscopy, were used to quantify and explain chain transfer to VOMM.

For contextual purposes the chapter summarizes the brief history of the VOMM use in emulsion polymerization. Again the rationale for polymerizing VOMMs in emulsions was to plasticize latex polymer particles to achieve lower minimum filming temperature (MFT) prior to coalescence, followed by increasing the glass transition temperature (T_g) after film formation via auto-oxidation. The approaches used to accomplish these objectives are outlined and compared. Side reactions occurring during polymerization are also discussed.
Chain transfer in solution polymerization systems was studied by polymerizing methyl methacrylate and butyl acrylate in the presence of a variety of vegetable oils, fatty acids, and vegetable oil derivatives. *In situ* FTIR spectroscopy was used to monitor acrylate conversion and determine the relative rates of polymerization. It was shown that tung oil completely stopped free radical chain polymerization due to its high α-eleostearic fatty acid content, which consists of 3 conjugated double bonds. Oleic acid, soybean oil, and linseed oil also retarded polymerization rates, with the extent of retardation increasing with the amount of unsaturation. Stearic acid was used as a control for chain transfer studies, as it does not possess allylic unsaturation.

NMR spectroscopy and GPC were used to determine the loci of chain transfer on the vegetable oils and derivatives. Chain transfer can occur either through the unsaturation or by abstraction of allylic hydrogen atoms, as illustrated in Figure 2-3, where $R'$ and $X'$ are initiator, monomer, and/or polymer radicals. NMR studies indicated little/no loss of vegetable oil unsaturation during the polymerization of methyl methacrylate in the presence of vegetable oil. GPC studies of the polymerization of methyl methacrylate in the presence of fluorescent tagged fatty acids suggested that the fatty acids did not covalently bind to the PMMA chains.
Chapter 7 investigates the affects of chain transfer via alternative model studies. These studies include the synthesis and evaluation of (meth)acrylic polymers in which the VOMMs are attached through a non-radical, post-polymerization process to avoid conflict with chain transfer during backbone synthesis. The model polymers provide benchmark data which can be used as a standard for further evaluation of VOMM-based emulsions, i.e., the most ideal plasticizer without any chain transfer or autooxidation prior to application. Methyl methacrylate, butyl acrylate, and 2-hydroxyethyl methacrylate were copolymerized and fatty acids with varying degrees of unsaturation were attached to the copolymer via dehydration with dicyclohexyl carbodiimide (DCC). FTIR spectroscopy, DMA, and gel content were performed on films drawn from the copolymers to determine the extent and nature of auto-oxidation for each sample.

Chapter 8 summarizes the major findings of this research. The behavior of vegetable oil unsaturation depends on the polymerization method, curing conditions, and comonomer composition. The results support the contention that if properly synthesized, VOMMs can be incorporated into oligomer and polymer

Figure 2-3. Reaction through double bond and with allylic hydrogen atoms.
main chains for use as renewable raw materials for application in high performance coatings.

Chapter 9 summarizes the author's current thoughts on potential research extensions and proposals complimentary to the completed dissertation. The potential detailed synthesis of novel VOMMs with lower viscosities for thiol-ene UV curable coatings is shown. An extension for chain transfer experimentation is presented. Finally, proposed research extensions for further model VOMM polymer studies include the development of post-polymerization reactions tailored to emulsions and a fundamental study of the post addition of fatty acids to emulsion polymers for idealized models capable of providing additional information on each of the major unknowns in this research area.
CHAPTER III
EXPERIMENTAL

Reagents

All reagents were purchased from or donated by several commercial vendors and are categorized by vendor name. Reagents were used without further purification unless otherwise noted. Solvents were purchased from Fisher Scientific and are not listed in this section.

Acros Organics: stearic acid, butyl acrylate (BA), phenothiazine (PTZ)
Alnor Oil: soybean oil, tung oil, soybean fatty acids, linseed fatty acids
Arista Industries: epoxidized soybean oil (ESO)
Bayer: isophorone diisocyanate (IPDI)
Ciba: Darocur® 1173
Dura Chemicals: 18% zirconium drier, cobalt drier
Fisher Scientific: methyl methacrylate (MMA)
Sigma-Aldrich: 2,2′-azobis(2-methylpropionitrile) (AIBN), 1,4-diazabicyclo[2.2.2]octane (DABCO), 2-hydroxyethyl acrylate (2-HEA), allyl alcohol (AA), 4-hydroxybutyl vinyl ether (4-HBVE), castor oil, dibutyltin dilaurate, trimethylolpropane tris(3-mercaptopropionate), Vectomer® 5015, trimethylolpropane triacrylate, 3-chloroperoxybenzoic acid, hydroquinone, oleic acid, linseed oil, PEG1000, 1-aminopyrene, dicyclohexylcarbodiimide (DCC),
dodecanethiol, 2-hydroxyethyl methacrylate (2-HEMA),
maleic anhydride, Brij® 92 (EO-5), Brij 72 (ES-5)

UCB: hexanediol diacrylate (HDDA)

Union Carbide: UVI®-6974

VOMM Characterization

Nuclear Magnetic Resonance (NMR) Spectroscopy

Proton ($^1$H) NMR spectroscopy was used to determine catalyst, reactant, monomer, and VOMM structure and functionality. $^1$H NMR solutions were obtained by dissolving 5-10 volume % of each reagent in deuterated chloroform (CDCl$_3$). Carbon ($^{13}$C) NMR and attached proton test (APT) NMR methods were used to characterize VOMM structure. In this work, quaternary and methylene sites were phased positive while methyl and methine sites were phased negative. $^{13}$C/APT NMR solutions were obtained by dissolving 20-40 volume % of VOMM in CDCl$_3$. $^1$H, $^{13}$C, and APT NMR were performed on a Varian Mercury Plus 300 MHz NMR spectrometer with relaxation delays ranging from 1 to 5 seconds and the number of scans ranging from 8 to 32 transients for $^1$H NMR and 64 to 1000 transients for $^{13}$C NMR.

Fourier Transform Infrared (FTIR) Spectroscopy

FTIR spectroscopy was used to determine VOMM reaction progress. Sample aliquots were taken at various times during the reaction and coated onto sodium chloride (NaCl) plates to be vertically placed in front of the IR beam within the FTIR spectrometer. FTIR spectra were obtained using a Varian 1000
Scimitar™ Series FTIR spectrometer at 2 cm⁻¹ resolution. Typically 32 scans were acquired for each spectrum.

**In-situ Fourier Transform Infrared Spectroscopy**

VOMM reaction progress was also monitored using a Mettler-Toledo ReactIR® 4000 equipped with a silicone composite (SiComp) attenuated total reflectance (ATR) probe. Data was collected at 4 cm⁻¹ resolution and 32 scans per data point. Profiles and data processing were performed using the ConcIRT software provided by Mettler-Toledo.

**Gel Permeation Chromatography (GPC)**

VOMM molecular weight and polydisperstiy was measured using GPC with an evaporative light scattering detector (ELSD) and refractive index (RI) detector. Samples were prepared by dissolving the VOMMs in THF at a concentration of 1-10 mg/mL.

**Polymer Characterization**

**Nuclear Magnetic Resonance (NMR) Spectroscopy**

Proton (¹H) NMR spectroscopy was used to determine the amount of unsaturation in vegetable oils before and after polymerization. ¹H NMR solutions were prepared by dissolving 1-5 volume % of polymer in CDCl₃.

**Gel Permeation Chromatography (GPC)**

The molecular weight and molecular weight distribution (MWD) of the (meth)acrylate polymers were determined via GPC using refractive index (RI) and ultraviolet (UV) detectors compared with polystyrene standards. Samples
were prepared by dissolving the polymers in THF at a concentration of 1-10 mg/mL.

*Dynamic Mechanical Analysis (DMA)*

DMA was conducted on a DMA Q800 from TA Instruments, Inc. utilizing tension mode analysis. The free films were approximately 1 mm thick x 5 mm wide. Data was recorded at frequencies of 1 Hz and 10 Hz (heating rate of 2°C/min from -50°C to 150°C). Three samples of each formulation were evaluated to ensure reproducibility and confidence. Molecular weight between crosslinks (M<sub>c</sub>) was calculated from the storage modulus minimum.

*Gel Content*

Gel content was obtained by fully immersing a known mass of cured material into methylene chloride for 24 hours at ambient temperature, followed by filtering, drying, and reweighing the solid remnants.

*Coating Characterization*

*Adhesion Crosshatch Tape Test (ASTM D 3359)*

Crosshatch adhesion was performed to test coating adhesion to cold-rolled steel test panels. A lattice pattern was made on the coating with six cuts in each direction perpendicular to the other. Pressure-sensitive tape was firmly applied over the lattice, allowed to remain for 60 seconds, and removed sharply at an angle of 180° to the coating surface. Adhesion was classified based on the film appearance after testing using the illustrations shown in Table 3-1.
Table 3-1. Crosshatch Adhesion Classification

<table>
<thead>
<tr>
<th>Classification</th>
<th>% Area Removed</th>
<th>Appearance</th>
</tr>
</thead>
<tbody>
<tr>
<td>5B</td>
<td>0%</td>
<td>![Image]</td>
</tr>
<tr>
<td>4B</td>
<td>&lt; 5%</td>
<td>![Image]</td>
</tr>
<tr>
<td>3B</td>
<td>5 - 15%</td>
<td>![Image]</td>
</tr>
<tr>
<td>2B</td>
<td>15 - 35%</td>
<td>![Image]</td>
</tr>
<tr>
<td>1B</td>
<td>35 - 65%</td>
<td>![Image]</td>
</tr>
<tr>
<td>0B</td>
<td>&gt; 65%</td>
<td>![Image]</td>
</tr>
</tbody>
</table>

*Rapid Deformation (ASTM D 2794)*

The rapid deformation test examines the ability of a coating to maintain its physical integrity and adhesion under impact. Test panels were placed in the apparatus with the coated side facing up for direct impact measurement. The indenter was gently lowered onto the panel while the weight was raised and dropped from a known height. The process was repeated to determine the height at which failure occurred. Coating failure is defined by the film cracking and delaminating from the substrate. The force at which the coating passes is recorded and ranges up to 160 lb-in of force.

*Conical Mandrel Flexibility (ASTM D 522-93a)*

The conical mandrel tests the coating resistance to cracking when flexed. The test is performed by placing the lever in the horizontal position while the test panel is positioned between the mandrel and the drawbar, finish side towards the drawbar. The panel is rigidly clamped adjacent to the mandrel. The lever is
rolled through 180° with uniform velocity to bend the specimen by approximately 135°. Coating elongation is determined by measuring the distance from the end of the crack to the small end of the mandrel. The mandrel diameter at which cracking ceased is recorded as the resistance to cracking value. The percent elongation curve is shown in Figure 3-1.

**Figure 3-1.** Percent elongation curve for conical mandrel flexibility.

**MEK Double Rub Solvent Resistance (PCI #8)**

Solvent resistance was tested using the Powder Coating Institute test, PCI #8. The rounded end of a 2 lb ballpeen hammer was covered with cheesecloth and soaked with methyl ethyl ketone (MEK). The cloth-covered end was brought in contact with the coating surface and rubbed back and forth (one double rub) without applying downward pressure on the hammer. The process was quantified as double rubs and ceased when the number of double rubs required to catastrophically break through the coating to the substrate occurred.

**Pencil Hardness (ASTM D3363)**

Pencil hardness testing is a rapid and inexpensive way to determine coating hardness using a set of pencil leads of known hardness. A pencil of
known hardness was held firmly against the coating at a 45° angle and pushed away in a ¼ inch stroke. The process was repeated with pencils of different hardness until a pencil that would not scratch/gouge the film was determined and the pencil hardness was then recorded. The pencil hardness scale is shown in Figure 3-2.

<table>
<thead>
<tr>
<th>6B</th>
<th>5B</th>
<th>4B</th>
<th>3B</th>
<th>2B</th>
<th>HB</th>
<th>F</th>
<th>H</th>
<th>2H</th>
<th>3H</th>
<th>4H</th>
<th>5H</th>
<th>6H</th>
</tr>
</thead>
<tbody>
<tr>
<td>Softer</td>
<td>Medium</td>
<td>Harder</td>
<td></td>
<td></td>
<td></td>
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<td></td>
<td></td>
<td></td>
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<td></td>
<td></td>
</tr>
</tbody>
</table>

**Figure 3-2. Pencil hardness scale.**

**Kinetics Analysis**

**In-situ Infrared Spectroscopy**

A ReactIR® 4000 (Mettler-Toledo) equipped with a diamond composite (DiComp) ATR probe was used to monitor acrylate polymerization. Data was collected at 4 cm\(^{-1}\) resolution and 32 scans per data point. Profiles and data processing was performed using ConcIRT software provided by Mettler-Toledo.

**Real Time Infrared (RTIR) Spectroscopy**

Functional group conversion for photopolymerizations was determined using RTIR spectroscopy. A modified Bruker 88 spectrometer with a horizontal transmission unit and a mercury cadmium telluride (MCT) detector was used in combination with a 200 watt high-pressure mercury-xenon lamp. UV light was piped from the light source to the sample chamber using a fiber optic cable. Samples were sandwiched between salt plates and irradiated for 5 minutes while simultaneously acquiring data.
CHAPTER IV
THIOL-ENE VOMM-BASED COATINGS

Introduction to Thiol-Ene Photopolymerization

UV curable coatings are typically VOC-free systems. Rapid ambient crosslinking permits increased line speed, reduced energy consumption, and low equipment space requirements.\(^1\) UV systems are employed for decorating and protecting diverse substrates such as computer chips, paper, optical fibers, composites, and automobile parts. Limitations of UV curable coatings include high material and equipment cost, curing limits with pigmented systems, poor three-dimensional curing, and sensitivity to oxygen (in free radically cured systems) and moisture (in cationically cured systems).

Oxygen inhibition has been mediated through a variety of methods including nitrogen blankets, \textit{in situ} oxygen barriers (e.g., paraffin wax), oxygen scavengers, and higher light intensity in UV curable coatings. Unfortunately, each of these techniques offers only limited protection and simultaneously increases overall coating costs. Cationically cured UV systems are insensitive to oxygen and replace free radically cured UV systems in certain specialty applications.\(^2\) However, cationic UV systems are inherently and extremely sensitive to nucleophilic agents such as water, even when present as ambient moisture.\(^3\) For historical and mechanistic reasons, cationic systems limit monomer variety and require longer UV exposure times.

UV curable chemistries based upon thiol-ene functionality offer a viable alternative to both free radical and cationic UV cured systems. They rapidly cure
at ambient temperature and are suitable with a wide variety of monomer choices, while remaining uninhibited by moisture and oxygen. Their unique curing mechanism promotes the formulation of thin film systems by selecting reactive components of the appropriate structure, functionality, and stoichiometry. Unfortunately, low molecular weight thiols typically possess unpleasant odors that have limited their commercial utilization.

The real benefit of thiol-ene curing chemistry lies in their robustness towards oxygen. In free radical systems, oxygen adds to the growing polymer chain to form an alkylperoxy radical that lacks sufficient energy to react with a monomeric double bond, thus retarding the polymerization process. In thiol-ene polymerizations, the alkylperoxy radicals are sufficiently reactive to abstract hydrogen atoms from thiols, thereby regenerating thiyl radicals and continuing the addition-chain transfer reaction. This specific mechanism is the major reason why thiol-ene photopolymerization has been so successful.

Figure 4-1 simplistically summarizes the thiol-ene reaction scheme for a monofunctional ene reacting with a monofunctional thiol. Linear thiol-ene polymers are formed by the reaction of difunctional thiols and enes, whereas crosslinked polymers are produced using thiols and enes of higher functionalities. Figure 4-2 shows the reaction of a thiol with an alkylperoxy radical.
Thiol-ene reaction scheme.

\[
\text{Int} \xrightarrow{\text{hv}} \text{Int}'
\]
\[
\text{Int}' + \text{RS-H} \rightarrow \text{SR} + \text{Int-H}
\]
\[
\text{RS'} + \text{R-S-CH}_2\dot{\text{CH}} \rightarrow \text{R-S-CH}_2\dot{\text{CH}}
\]
\[
\text{R-S-CH}_2\dot{\text{CH}} + \text{RS-H} \rightarrow \text{R-S-CH}_2\dot{\text{CH}}_2 + \text{RS'}
\]
\[
2 \text{RS'} \rightarrow \text{RS-SR}
\]
\[
2 \text{R-S-CH}_2\dot{\text{CH}} \rightarrow \text{R-S-CH}_2\dot{\text{CH}}_2\dot{\text{CH}}_2\dot{\text{CH}}_2\dot{\text{S-R}}
\]

Figure 4-1. Thiol-ene reaction scheme.

Reaction of an alkylperoxy radical with thiol.

Thiol-ene UV curable coatings typically contain a prepolymer, reactive diluent, thiol, and photoinitiator. The prepolymer component is most often a petrochemical derivative. Our research efforts have focused on developing vegetable oil macromonomers (VOMMs) polymerizable via free radical mechanisms. VOMMs are “green chemistry” monomers proposed as biobased alternatives to crude oil-based materials. The benefits of VOMM-based emulsions in waterborne architectural coatings include renewable resource utilization, fatty acid plasticization for VOC-free coalescence, and the opportunity for post-application crosslinking of dried films via auto-oxidation. Many authors
have reported the use of vegetable oils as feedstock for UV curable coatings and composites.\textsuperscript{6-10} This chapter reviews the synthesis, characterization, and test results for a series of vinyl ether, allyl ether, and acrylate functional VOMMs derived from soybean oil and castor oil for use in thiol-ene UV curable coatings. Reaction kinetics were obtained via \textit{in situ} infrared monitoring. Coating post-cure tests included crosshatch adhesion, solvent resistance, pencil hardness, rapid deformation, and conical mandrel flexibility. Dynamic mechanical analysis (DMA) and Fourier transform infrared (FTIR) spectroscopy were used to quantify crosslinking that occurred after the initial UV exposure.

\textbf{Soybean Oil VOMM Synthesis and Characterization}

Vegetable oils are good feedstocks for chemical modification due to the presence of internal unsaturation, allylic hydrogen atoms, and ester linkages. Knot reviewed numerous chemical modifications of vegetable oils.\textsuperscript{11} One such modification, termed the ene reaction, involves the reaction of maleic anhydride with a double bond. Unsaturated oils, such as linseed oil, are reported to readily react with maleic anhydride at 230°C to form succinic anhydride moieties.\textsuperscript{12} Maleic anhydride will also undergo Diels-Alder cycloaddition reactions with conjugated unsaturation. The ene and Diels-Alder reaction (Figure 4-3) are catalyzed by Lewis acids such as AlCl\textsubscript{3}.\textsuperscript{13,14} Additionally, some thermal polymerization, otherwise known as heat bodying, commonly occurs when vegetable oils are heated to high temperatures.
Figure 4-3. Ene and Diels-Alder reaction mechanisms, respectively.

Soy VOMMs were prepared by a one pot, two-step process. In the first step, maleinized soybean oil (MSO) was synthesized by reacting maleic anhydride with soybean oil (iodine value ranging from 120-141) at a 2:1 molar ratio. Next, 2-HEA, AA, and 4-HBVE were each reacted with MSO via ring-opening esterification to create the acrylic, allylic, and vinyl ether half-esters, respectively.

**MSO Synthesis**

100 g (0.114 mole) of soybean oil and 22.32 g (0.228 mole) of maleic anhydride were added to a 500 mL round bottom flask. The round bottom flask was equipped with a mechanical stirrer, water condenser, and a nitrogen purge needle. The contents were stirred and purged with nitrogen for 24 hours prior to reaction. The mixture was heated to 230°C for 3 hours. A color change, light yellow to dark orange, was noted at 215°C as conjugation in the oil increased with the formation of MSO (Figure 4-4).
Acrylate Soy VOMM

0.8 g (6.98 mmole) of 2-HEA, 10.0 g (9.3 mmole) of MSO, and 108 mg (0.96 mmole, 1 wt %) of DABCO catalyst were blended in a scintillation vial using a small magnetic stir bar. The solution was heated to 60°C for 4 hours to obtain the half-ester through an esterification reaction (Figure 4-5).

Allyl Soy VOMM

0.4 g (6.98 mmole) of AA, 10.0 g (9.3 mmole) of MSO, and 104 mg (0.92 mmole, 1 wt %) of DABCO catalyst were blended in a scintillation vial using a
small magnetic stir bar. The solution was heated to 60°C for 4 hours to produce the half-ester through an esterification reaction (Figure 4-6).

![Figure 4-6. Allyl soy VOMM structure.](image)

Vinyl Ether Soy VOMM

0.8 g (6.98 mmole) of 4-HBVE, 10 g (9.3 mmole) of MSO, and 108 mg (0.96 mmole, 1 wt %) of DABCO catalyst were blended in a scintillation vial using a small magnetic stir bar. The solution was heated to 60°C for 4 hours to produce the half-ester through an esterification reaction (Figure 4-7).

![Figure 4-7. Vinyl ether soy VOMM structure.](image)

Unfortunately, the vinyl ether soy VOMM crosslinked in the reaction flask every time during synthesis, which resulted in an unusable product. This is
presumably due to cationic polymerization of the vinyl ether initiated by the carboxylic acids that form upon ring opening of succinic anhydride. All attempts to remedy this problem proved futile, and the synthesis of vinyl ether soy VOMM was abandoned. The acrylate soy VOMM and allyl soy VOMM prepolymers were formulated into thiol-ene UV curable coatings to establish proof-of-concept. Upon UV irradiation, however, the films cured only at the surface, yielding a tacky, wrinkled film with liquid still present at the coating/metal substrate interface. Coating failure was attributed to the high amount of conjugated double bonds in the prepolymer which stabilized the initiating/propagating radicals and retarded polymerization. Partial cure occurred at the surface due to the higher concentration of photons from the UV light source at the surface. Thus, soybean oil was abandoned as a feedstock for prepolymers for thiol-ene UV curable coatings, and new monomers based on castor oil were synthesized.

**Castor Oil VOMM Synthesis and Characterization**

Castor oil is a very useful vegetable oil for VOMM synthesis as the triglyceride is composed of approximately 90% ricinoleic acid. Integration of the $^1$H NMR spectrum of castor oil gave a value of 93% ricinoleic acid (figure 4-8). This corresponds to 2.7 - 2.8 hydroxyls per molecule and potentially a 2.7 or 2.8 functional VOMM. While vinyl functionality can be introduced in castor oil using various methods, urethane chemistry was chosen as it produces tough coatings with good hydrolytic stability, abrasion, chemical, and solvent resistance properties.
Castor VOMMs were synthesized by reacting hydroxyl functional monomers with IPDI followed by reaction with castor oil (iodine value ranging from 83-88) (Figure 4-9). In the APT NMR spectrum (Figure 4-10), peak 13 is of special interest because it corresponds to the hydroxyl methine carbon of ricinoleic acid. This peak shifts from 71.5 ppm to 74.3 ppm when the hydroxyl reacts with an isocyanate to form a urethane group. Solvents, catalysts, reaction temperature, order of addition, and stoichiometry were investigated to optimize the synthesis of castor VOMMs. It was determined that well-performing castor VOMMs could be synthesized using hexane as the solvent, DBTDL as the catalyst, and reacting the hydroxyl functional monomers with IPDI at
approximately 0°C before reacting with castor oil at 50°C, and overindexing (i.e.,
reacting in stoichiometric excess) the hydroxyl monomers and IPDI.

Figure 4-9. Castor VOMM synthesis.
Hexane is a relatively non-polar solvent that increases the reactivity of hydroxyls towards isocyanates, thereby yielding favorable reaction times. Polar solvents such as methylene chloride have high solvency for urethanes but dramatically slow down the reaction.

DBTDL was chosen as a catalyst for the reaction due to its regioselectivity in urethane reactions. In the presence of this Lewis acid catalyst, the 2° isocyanate is rendered 11.5 times more reactive towards alcohols than the 1° isocyanate. Consequently, the monomer hydroxyls react almost exclusively with the 2° isocyanate of IPDI, leaving the 1° isocyanate free to react with the 2° hydroxyls of castor oil. Lewis bases, such as DABCO, are known to reverse the
reactivity, with $1^\circ$ isocyanates having greater reactivity over $2^\circ$. However, the regioselectivity is much less than that seen with DBTDL.

Reaction temperature affects the catalyst activity and the reactivity of the hydroxyl/isocyanate reaction. Initially, low temperatures were used to promote the hydroxyl reactivity towards the $2^\circ$ isocyanate. Higher reaction temperatures were used when reacting the residual $1^\circ$ isocyanate with castor oil as selectivity was no longer an issue at this stage of the synthesis. Higher temperatures also assisted in reducing the system viscosity which had increased due to hydrogen-bonding effects.

Order of addition is a critical parameter, since it determines the final VOMM structure and properties. The hydroxyl functional vinyl monomers (VM) were added dropwise to IPDI to yield the dimer (VM-IPDI) and limits the production of the trimer, VM-IPDI-VM. THE VM-IPDI adduct was then reacted with castor oil. Reacting castor oil with IPDI in the first step would have resulted in the formation of a highly viscous, partially crosslinked polymer. This order of addition also limited crosslinking between triglycerides.

Inevitably, some trimers (e.g., acrylated trimer, Figure 4-11) were formed during the reaction despite careful control of solvent, catalyst, reaction temperature, and order of addition. Consequently, stoichiometric proportions of each reactant would result in incomplete functionalization of castor oil due to insufficient isocyanate concentration at the beginning of the second reaction stage. Therefore, excess hydroxyl monomers and IPDI are used to ensure appropriate isocyanate concentration for the second stage.
Figure 4-11. Acrylated trimer structure.

Acrylate Castor VOMM

69.38 g (0.313 mole) of IPDI, 2.23 g (7.9 mmole, 0.2 wt%) of DBTL, 0.56 g (5 mmole, 500 ppm) of HQ, and 100 mL of hexane were added to a 500 mL three-neck round bottom flask equipped with a thermocouple, addition funnel, and magnetic stir bar. The solution was stirred and cooled to approximately 0°C using an ice bath. 38.75 g (0.334 mole) of 2-HEA was added dropwise to the flask via an addition funnel. The reaction was warmed to 50°C for 1 hr before adding 100 g (0.108 mole) of castor oil. The reaction was monitored using the ReactIR™4000 (Figure 4-12) and continued until the isocyanate had fully reacted. The isocyanate and urethane peaks were observed at 2270 cm⁻¹ and 1705 cm⁻¹, respectively. Graph discontinuities are attributed to increasing temperature near the end of stage one as well as peak dilution as castor oil was added in stage two. Hexane was removed in vacuo. The reaction product (Figure 4-13) was characterized by APT NMR spectroscopy (Figure 4-14).
Figure 4-12. Acrylate castor VOMM isocyanate and urethane peaks, respectively.

Figure 4-13. Acrylate castor VOMM structure.
Allyl Castor VOMM

69.38 g (0.313 mole) of IPDI, 2.23 g (7.9 mmole, 0.2 wt%) of DBTL, 0.56 g (5 mmole, 500 ppm) of HQ, and 100 mL of hexane were added to a 500 mL three-neck round bottom flask equipped with a thermocouple, addition funnel, and magnetic stir bar. The reaction contents were stirred and cooled to approximately 0°C using an ice bath. 19.38 g (0.334 mole) of AA were added dropwise to the flask via an addition funnel. The reaction was warmed to 50°C for 1 hr before adding 100 g (0.108 mole) of castor oil. The reaction was monitored using the ReactIR 4000 (Figure 4-15) and continued until the isocyanate had fully reacted. Hexane was removed in vacuo. The reaction product (Figure 4-16) was characterized by APT NMR spectroscopy (Figure 4-17).
Figure 4-15. Allyl castor VOMM isocyanate and urethane peaks, respectively.

Figure 4-16. Allyl castor VOMM structure.
Figure 4-17. APT NMR spectrum of allyl castor VOMM.

Vinyl Ether Castor VOMM

69.38 g (0.313 mole) of IPDI, 2.23 g (7.9 mmole, 0.2 wt%) of DBTL, 0.56 g (5 mmole, 500 ppm) of HQ, and 100 mL of hexane were added to a 500 mL three-neck round bottom flask equipped with a thermocouple, addition funnel, and magnetic stir bar. The solution was stirred and cooled to approximately 0°C using an ice bath. 38.75 g (0.334 mole) of 4-HBVE were added dropwise to the flask via an addition funnel and warmed to 50°C for 1 hr before adding 100 g (0.108 mole) of castor oil. The reaction was monitored using the ReactIR 4000 (Figure 4-18) and allowed to continue until the isocyanate had fully reacted. Hexane was removed in vacuo. The reaction product (Figure 4-19) was characterized by APT NMR spectroscopy (Figure 4-20).
Figure 4-18. Vinyl ether castor VOMM isocyanate and urethane peaks, respectively.

Figure 4-19. Vinyl ether castor VOMM structure.
Figure 4-20. APT NMR spectrum of vinyl ether castor VOMM.

Gel Permeation Chromatography

The castor VOMMs were analyzed along with castor oil to determine the product distribution. In addition to the ideal structure proposed for each castor VOMM, there appeared a low molecular weight peak and a high molecular weight shoulder. The low molecular weight peak is due to the VM-IPDI-VM trimer, and the high molecular weight peak can be attributed to castor oil dimers/trimers. The major product is the vinyl functionalized castor oil macromolecules, which are higher in molecular weight than castor oil. The composite GPC chromatogram is shown in figure 4-21.
Figure 4-21. GPC traces of the castor VOMMs.

Table 4-1 shows the distribution of peaks a, b, and c, corresponding to the low molecular weight trimers, major VOMM product, and high molecular weight castor adducts, respectively.

Table 4-1. Product Distribution in Castor VOMMs

<table>
<thead>
<tr>
<th>VOMM</th>
<th>Peak a</th>
<th>Peak b</th>
<th>Peak c</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acrylate</td>
<td>20%</td>
<td>63%</td>
<td>17%</td>
</tr>
<tr>
<td>Allyl Ether</td>
<td>15%</td>
<td>70%</td>
<td>15%</td>
</tr>
<tr>
<td>Vinyl Ether</td>
<td>17%</td>
<td>72%</td>
<td>11%</td>
</tr>
</tbody>
</table>

Peaks a, b, and c had average molecular weights of 330 g/mol, 2,460 g/mol, and 4,625 g/mol, respectively. The molecular weights were taken from the maximum value in each peak (M_p). The data does not represent exact molecular weights for products under each peak, due to calibration with polystyrene standards, but only serves to show relative values among peaks.
Thiol-Ene Composition

The synthesized castor VOMMs were formulated into thiol-ene UV curable coatings and evaluated for film performance. Castor VOMMs and TMPTA were blended at a 4:1 weight fraction under high shear for 2 minutes with 2 parts per hundred resin (phr) Darocur 1173 added as the photoinitiator. Additionally, three versions were formulated with 0.25 wt % of zirconium drier (18% Zr) as a catalyst for auto-oxidation (Table 4-2). Preliminary results on mixtures containing zirconium and cobalt driers did not cure well, presumably because the cobalt drier competitively absorbed UV light. The coatings were applied on cold rolled steel Q-panels at 3 mils wet film thickness and cured on a Fusion UV system conveyor line equipped with a Fusion D bulb. The films were passed through the conveyor line five times at a speed of 567 ft/min.

Table 4-2. Thiol-Ene UV Curable Formulation

<table>
<thead>
<tr>
<th>Formulation</th>
<th>Castor-VOMM</th>
<th>VOMM (g)</th>
<th>Thiol (g)</th>
<th>Photoinitiator (g)</th>
<th>Zr Drier (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Vinyl ether</td>
<td>32</td>
<td>8</td>
<td>0.8</td>
<td>0.1</td>
</tr>
<tr>
<td>2</td>
<td>Vinyl ether</td>
<td>32</td>
<td>8</td>
<td>0.8</td>
<td>No drier</td>
</tr>
<tr>
<td>3</td>
<td>Allyl</td>
<td>32</td>
<td>8</td>
<td>0.8</td>
<td>0.1</td>
</tr>
<tr>
<td>4</td>
<td>Allyl</td>
<td>32</td>
<td>8</td>
<td>0.8</td>
<td>No drier</td>
</tr>
<tr>
<td>5</td>
<td>Acrylate</td>
<td>32</td>
<td>8</td>
<td>0.8</td>
<td>0.1</td>
</tr>
<tr>
<td>6</td>
<td>Acrylate</td>
<td>32</td>
<td>8</td>
<td>0.8</td>
<td>No drier</td>
</tr>
</tbody>
</table>

Real Time FTIR Analysis of Initial Cure

The initial rate of conversion of functional groups was determined using Real Time FTIR spectroscopy. Samples were irradiated for 5 minutes. Data was collected during irradiation. Conversion was determined using equation 4-1, where \( C_t \) is the conversion at time \( t \), \( A_o \) is the initial absorbance, and \( A_t \) is the absorbance at time \( t \). Figure 4-22 shows the percent conversion plot for
formulation 1. The vinyl ether (1622 cm$^{-1}$ C=C stretch)$^{17}$ continued to react until 85% conversion, while the thiol (2575 cm$^{-1}$ S-H stretch)$^{17}$ reacted until 75% conversion was obtained at the end of 5 minutes. Since vinyl ethers usually react stoichiometrically with thiols, the disparity between the two reactive moieties indicate another reaction mechanism is present.

$$C_t = \left( \frac{A_0 - A_t}{A_0} \right) \times 100$$

Equation 4-1. Conversion equation.

Figure 4-22. Formulation 1 initial functional group conversions.

Figure 4-23 shows the percent conversion plot for formulation 2. Similar to formulation 1, higher conversion was noted for vinyl ethers (85%) than the thiol (70%) at the end of 5 minutes of irradiation, suggesting again the presence of an additional curing mechanism such as copolymerization with another functional group.
Formulations 3 and 4 exhibited much lower ene conversion than formulations 1 and 2 (Figures 4-24 and 4-25, respectively). Allyl ether (3075 cm\(^{-1}\) =CH\(_2\) stretch\(^{17}\)) conversion began to level off after 100 seconds, while the thiol continued to react.

Figure 4-23. Formulation 2 initial functional group conversions.

Figure 4-24. Formulation 3 initial functional group conversions.
Figures 4-26 and 4-27 show the conversion plots for formulations 5 and 6, respectively. In both systems, the acrylate (810 cm$^{-1}$ C-H bend$^{17}$ reached 90% conversion, the thiol, 60% conversion. The disparity between the ene and thiol disappearance/reactivity was expected, as acrylates are known to undergo significant homopolymerization even in the presence of thiol-ene photopolymerization.
Figure 4-26. Formulation 5 initial functional group conversions.

Figure 4-27. Formulation 6 initial functional group conversions.

Coating Post-Cure Testing

Coating post-cure tests included crosshatch adhesion (ASTM D 3359), MEK resistance (PCI #8), pencil hardness (ASTM D 3363), rapid deformation (ASTM D 2794), and conical mandrel (ASTM D 1737). Coatings were applied to
cold rolled steel Q-panels and tested immediately after UV curing and 1 week after UV exposure. The test results are shown in Table 4-3.

Table 4-3. ASTM Post-Cure Test Results

<table>
<thead>
<tr>
<th>Formulation</th>
<th>1 week</th>
<th>1 week</th>
<th>1 week</th>
<th>1 week</th>
<th>1 week</th>
<th>1 week</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thickness (mils)</td>
<td>1.65</td>
<td>1.49</td>
<td>1.39</td>
<td>1.34</td>
<td>1.47</td>
<td>1.76</td>
</tr>
<tr>
<td>MEK Double Rubs</td>
<td>114</td>
<td>145</td>
<td>127</td>
<td>154</td>
<td>108</td>
<td>176</td>
</tr>
<tr>
<td>Adhesion</td>
<td>2B</td>
<td>5B</td>
<td>2B</td>
<td>3B</td>
<td>5B</td>
<td>5B</td>
</tr>
<tr>
<td>Pencil Hardness</td>
<td>F</td>
<td>3H</td>
<td>F</td>
<td>2H</td>
<td>F</td>
<td>5H</td>
</tr>
<tr>
<td>Direct Impact (in-lbs)</td>
<td>120</td>
<td>120</td>
<td>160</td>
<td>160</td>
<td>140</td>
<td>160</td>
</tr>
<tr>
<td>Flexibility (% Elongation)</td>
<td>28</td>
<td>28</td>
<td>28</td>
<td>28</td>
<td>28</td>
<td>28</td>
</tr>
</tbody>
</table>

All the coatings displayed the maximum measurable flexibility (28% elongation), which is unusual since UV curable coatings often have low flexibility. More importantly, while the maximum measurable flexibility remained unchanged, continued curing resulted in other property enhancement upon 1 week of aging. For instance, formulation 1 registered increase in MEK double rubs from 114 to 145, increase in adhesion rating from 2B to 5B, and an increase in pencil hardness from F to 3H. Other formulations also showed a similar trend of increasing solvent resistance, adhesion, and hardness with aging. In particular, formulations 5 and 6 showed a drastic impact resistance increase, rising from 30 to 160 in-lbs and 40 to 160 in-lbs, respectively.

DMA and Gel Content

Further analysis was needed to determine the specific network and the remaining sol fraction. Thus, DMA and gel content studies were performed to...
quantify the crosslink density of the six coating formulations at a specific point in time after a given UV cure. The breadth of the tan δ curve is a measure of the heterogeneity of the crosslinked network, while the temperature corresponding to the tan δ peak yields the DMA Tg. The storage modulus minimum was used to calculate the molecular weight between crosslinks (M_c) using equation 4-2, where δ is the bulk density (in g/cm³), R is the gas constant (8.314 J/K*mol), E' is the storage modulus minimum (in MPa), and T is the corresponding temperature (in Kelvin).\(^{18}\)

$$M_c = \frac{3 \ast 5 \ast R \ast T}{E'}$$  

**Equation 4-2. Molecular weight between crosslinks equation.**

Figures 4-28 and 4-29 show the tan δ and storage modulus plots, respectively, for the initial measurements. Formulations 1 and 2 have the highest and narrowest tan δ peaks, indicating they have the most homogeneous networks of all the formulations tested. This is explained in terms of the vinyl ethers' reactivity with the thiol. Due to the oxygen atom's effect on resonance stability, vinyl ethers do not undergo free radical homopolymerization but instead copolymerize in an alternating manner with other free radical comonomers and homopolymerize when cured cationically. Vinyl ethers also readily react with thiyl radicals as they are relatively electronegative (due to the increased π-system effect of oxygen) and thiols are relatively electropositive. Formulations 4, 5, and 6 (containing allyl ether and acrylate functional groups) exhibited shorter and broader tan δ peaks than formulations 1 and 2, indicating increased
heterogeneity in the network. Allyl ethers and especially acrylates undergo homopolymerization in addition to reacting with thiols. These dual cure mechanisms increase the complexity of the crosslinked network. Formulation 3 exhibited two tan δ peaks, assigned to the formation of two concurrent networks. Since an allyl ether is a terminal double bond, it is more reactive than the internal double bond due to reduced steric hindrance. Zirconium driers are expected to increase the radical reactivity of both double bonds, so the difference in reactivity may not be as significant.

![Figure 4-28. Tan δ after initial cure.](image)

Each resulting coating, with the exception of formulation 3, exhibited log storage modulus minimums from 1 to 10. Formulation 3 had the largest width at half height, indicating a very heterogeneous crosslinked network. In addition,
formulation 3 possessed the lowest solvent resistance, indicating lowest crosslink
density. Here the increased reactivity of the internal unsaturation gelled the
system at a lower conversion than formulation 4, causing early vitrification and
creating diffusional limits to further propagation, i.e., leading to a lower initial
crosslink density.

![Log storage modulus at linear plateau after initial cure.](image)

**Figure 4-29.** Log storage modulus at linear plateau after initial cure.

Table 4-4 shows the DMA and gel content data for the formulations tested
immediately after cure and after one week of postcure. The general trend of
increased crosslink density upon postcure was noted for all formulations,
especially for formulation 3. This increase resulted from continued reaction of
functional groups in the coating over time, a phenomenon known as dark cure.
However, auto-oxidation may also be responsible for some of the increased
crosslink density. The increased crosslink density corroborates well with the improved hardness and solvent resistance of the coatings in macroscopic testing data. Flexibility decreases with increased hardness as a general rule, but the vegetable oil fatty acid tails plasticize the films and allow them to retain their original flexibility. The improved adhesion may be due to further substrate wetting and stress release within the film and migration of urethane functionality to the coating/substrate interface upon aging.

Table 4-4. Gel Content and $M_c$ Data

<table>
<thead>
<tr>
<th>Formulation</th>
<th>Time</th>
<th>Gel Content (%)</th>
<th>$M_c$ (g/mol)</th>
<th>$\Delta M_c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
<td>86</td>
<td>2,594 ± 463</td>
<td>11.1%</td>
</tr>
<tr>
<td></td>
<td>1 week</td>
<td>91</td>
<td>2,305 ± 236</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>0</td>
<td>86</td>
<td>3,134 ± 165</td>
<td>21.5%</td>
</tr>
<tr>
<td></td>
<td>1 week</td>
<td>92</td>
<td>2,460 ± 62</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>0</td>
<td>69</td>
<td>23,716 ± 6,491</td>
<td>65.7%</td>
</tr>
<tr>
<td></td>
<td>1 week</td>
<td>85</td>
<td>8,137 ± 2,386</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>0</td>
<td>74</td>
<td>9,115 ± 900</td>
<td>15.9%</td>
</tr>
<tr>
<td></td>
<td>1 week</td>
<td>90</td>
<td>7,665 ± 1,172</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>0</td>
<td>92</td>
<td>1,521 ± 154</td>
<td>11.2%</td>
</tr>
<tr>
<td></td>
<td>1 week</td>
<td>97</td>
<td>1,691 ± 545</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>0</td>
<td>91</td>
<td>1,435 ± 101</td>
<td>25.7%</td>
</tr>
<tr>
<td></td>
<td>1 week</td>
<td>93</td>
<td>1,804 ± 542</td>
<td></td>
</tr>
</tbody>
</table>

FTIR Postcure Analysis

FTIR analysis helped delineate between postcure thiol-ene reaction and auto-oxidation. Vinyl ether (1622 cm$^{-1}$), acrylate (810 cm$^{-1}$), thiol (2575 cm$^{-1}$), allyl ether (3075 cm$^{-1}$), and cis-unsaturation (3010 cm$^{-1}$, C-H stretch)$^{17}$ peaks
were monitored before cure, immediately after cure, and after 1 week of postcure. Percent conversion was determined for all the functional groups except cis-unsaturation, as its peak exists overlaps with another peak, making accurate integration difficult (Figure 4-30).

![Figure 4-30. FTIR spectra showing cis-unsaturation peak.](image)

The percent of vinyl ether conversion in formulation 1 was characterized by a high initial conversion followed by a small amount of postcure (Figure 4-31). Similar behavior was observed with thiols (Figure 4-32). Figure 4-33 reveals significant conversion of cis-unsaturation immediately after cure but insignificant change during postcure.
Figure 4-31. Formulation 1 vinyl ether conversion.

Figure 4-32. Formulation 1 thiol conversion.
Figure 4-33. Formulation 1 cis-unsaturation conversion.

Vinyl ether, thiol, and cis-unsaturation conversions of formulation 2 are shown in Figures 4-34, 4-35, and 4-36, respectively. Reaction behavior for formulation 2 is similar to that of formulation 1, except for slightly greater postcure.
Figure 4-34. Formulation 2 vinyl ether conversion.

Figure 4-35. Formulation 2 thiol conversion.

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Allyl ether, thiol, and cis-unsaturation FTIR spectra for formulations 3 and 4 are shown in Figures 4-37 to 4-42. Formulations 3 and 4 exhibited lower conversion of allyl ether functionality than the vinyl ether systems. However, significant reduction of the thiol peak was observed during postcure. Allyl ethers are much less reactive towards thiol-ene polymerization than vinyl ethers. Formulation 3 was characterized by a very large reduction in cis-unsaturation upon cure, possibly due to auto-oxidation promoted by the Zr drier.
Figure 4-37. Formulation 3 allyl ether conversion.

Figure 4-38. Formulation 3 thiol conversion.
Figure 4-39. Formulation 3 cis-unsaturation conversion.

Figure 4-40. Formulation 4 allyl ether conversion.
Figure 4-41. Formulation 4 thiol conversion.

Figure 4-42. Formulation 4 cis-unsaturation conversion.
Acrylate, thiol, and cis-unsaturation conversions of formulation 5 are shown in Figures 4-43, 4-44, and 4-45, respectively. Significant conversion is noted for all functional groups, with acrylate and thiol groups undergoing relatively large postcure. Acrylate conversion is much higher than that of thiols, since acrylates undergo homopolymerization in addition to thiol-ene step-growth polymerization. Less cis-unsaturation conversion was noted for formulation 5.

Figure 4-43. Formulation 5 acrylate conversion.
Figure 4-44. Formulation 5 thiol conversion.

Figure 4-45. Formulation 5 cis-unsaturation conversion.

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Acrylate, thiol, and cis-unsaturation conversions for formulation 6 are shown in Figures 4-46, 4-47, and 4-48, respectively. Formulation 6 behaved very similar to formulation 5 where there was disproportionate conversion of acrylate and thiol groups, however, they did not undergo the same level of conversion. Formulation 6 exhibited less initial conversion and postcure. The cis-unsaturation remains relatively unchanged throughout the entire reaction.

Figure 4-46. Formulation 6 acrylate conversion.
Figure 4-47. Formulation 6 thiol conversion.

Figure 4-48. Formulation 6 cis-unsaturation conversion.
Figure 4-49 shows percent conversions (calculated from FTIR spectra) for the ene and thiol functional groups of each formulation immediately after cure as well as 1 week of postcure. All the formulations exhibited increased functional group conversion with time. Percent conversion for vinyl ether was higher than thiol conversion for formulations 1 and 2, indicating copolymerization of vinyl ethers with cis-unsaturation. Formulations 3 and 4 had the lowest percent conversions (evidenced by their relatively low gel contents), with higher percent conversions observed for thiols than the allyl ether groups. Here cis-unsaturation reacted competitively with thiols in these systems. There is less differentiation between allyl ethers and cis-unsaturation, since allyl ethers are terminal double bonds and are thus similar chemically to internal double bonds. Formulations 5 and 6 showed a large difference between acrylate and thiol functional group conversion, due to acrylates participating in homopolymerization as well as copolymerization with thiol-enes.
Figure 4-49. Summary of postcure conversions.

It is apparent from the DMA and FTIR data that the curing behaviors of these VOMM-based thiol-ene systems are complicated. The concurrent reaction mechanisms cause deviations from ideal network uniformity by varying degrees. Therefore model networks were created in order to have a standard by comparisons could be made. These model networks were composed of low molecular weight multifunctional thiols and enes of high purity.

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Ideal Networks

Thiol-ene networks are unique as they have been used to form some of the most uniform crosslinked polymeric networks known. The uniform crosslink densities exhibited by these systems are attributed to the radical step-growth process. Propagation involves two steps; the addition of a thiyl radical to a vinyl monomer, followed by subsequent chain transfer of a thiol hydrogen to the alkyl radical, leading to the formation of a thioether and a thiyl radical. It should be noted that homopolymerization is a competing reaction. However some enes, such as vinyl ethers, will selectively undergo only the thiol-ene reaction. Model systems were prepared as a comparative tool for thiol-ene systems containing VOMMs.

Formulation 7 contained equimolar amounts of trivinyl ether (Vectomer® 5015) and trithiol (trimethylolpropane tris(3-mercaptopropionate)). Formulation 8 contained equimolar amounts of triacrylate (trimethylolpropane triacrylate) and trithiol functional groups, while formulation 9 contained 0.5 equivalents of trivinyl ether, 0.5 equivalents of triacrylate, and 1 equivalent of trithiol (Table 4-5). All formulations contained 2 phr Darocur 1173. The reagents were blended at high shear (2150 rpm) for 1 minute prior to reaction.

<table>
<thead>
<tr>
<th>Formulation</th>
<th>Ene</th>
<th>Trithiol</th>
<th>Darocur 1173</th>
</tr>
</thead>
<tbody>
<tr>
<td>7</td>
<td>Trivinyl ether</td>
<td>4.00 g</td>
<td>3.16 g</td>
</tr>
<tr>
<td>8</td>
<td>Triacrylate</td>
<td>2.35 g</td>
<td>3.16 g</td>
</tr>
<tr>
<td>9</td>
<td>Trivinyl ether</td>
<td>2.00 g</td>
<td>3.16 g</td>
</tr>
<tr>
<td></td>
<td>Triacrylate</td>
<td>1.17 g</td>
<td></td>
</tr>
</tbody>
</table>
The percent conversion plot of formulation 7 (Figure 4-50) shows equal consumption of vinyl ether and thiol functional groups, indicating a strict adherence to the thiol-ene step growth mechanism and no deviation due to homopolymerization. This was expected, since vinyl ethers are known to only homopolymerize cationically.

![Graph showing percent conversion over time with vinyl ether and thiol conversion tracked.]

Figure 4-50. Formulation 7 functional group conversions.

Figure 4-51 shows the triacrylate-trithiol (formulation 8) conversion plot. In contrast to Figure 4-50, a large disparity between acrylate and thiol conversion is observed due to competition between thiol-ene step growth addition and acrylate homopolymerization. Nearly 50% of thiol functional groups remain unreacted due to the stoichiometric imbalance created by polymer radicals preferring acrylate double bond addition over thiol hydrogen abstraction.
Figure 4-51. Formulation 8 functional group conversions.

Figure 4-52 shows nearly 75% conversion of thiol in the triacrylate-trivinyl ether-trithiol system (formulation 9). Here acrylate groups are completely consumed. The vinyl ether reaction is presumed to have proceeded to near completion. However, the extent of vinyl ether conversion is unknown, however, due to the overlap of vinyl ether and acrylate peaks at 1640 cm$^{-1}$.
Figure 4-52. Formulation 9 functional group conversions.

Gel content was determined in order to corroborate the above mentioned RTIR results. All formulations formed high gel fractions, with 100% gel content observed for formulation 7, 95.4% for formulation 8, and 99.6% for formulation 9.

For DMA analysis, free films were generated by pouring the formulations into 1 mm deep silicon molds and curing them via a Fusion UV system conveyor line equipped with a Fusion D bulb. Figure 4-53 overlays the tan δ peaks for all three formulations. The thiol-vinyl ether system displayed the narrowest tan δ (width at half-height approximately 10°C) and the lowest $T_g$ ($\tan \delta_{\text{MAX}}$ of -5°C) due to strict adherence to the thiol-ene polymerization mechanism. The thiol-vinyl ether-acrylate mixed system (width at half-height at approximately 20°C) possessed a higher tan $\delta_{\text{MAX}}$ temperature due to the higher acrylate $T_g$. The
thiol-acrylate system's tan δ_{MAX} temperature is even higher and the largest width at half-height (approximately 30°C). This supports multiple mechanisms for cure, resulting in a heterogeneous crosslinked network. The width at half-height for the Castor-VOMM thiol-ene formulations ranged from 30°C to 50°C, indicating a crosslinked network with even greater heterogeneity.

![Graph of tan δ vs Temperature](image)

**Figure 4-53. Model network tan δ peaks.**

Thiol-ene UV curable coatings incorporating VOMMs as prepolymers are useful for applications requiring good flexibility throughout the coating's lifetime. In general, the "dark cure" phenomenon is a challenge for formulators, since continued crosslinking after UV exposure results in increased hardness and reduced flexibility. The lower quantity of allylic unsaturation present in castor-based VOMMs produced networks with better plasticizers (Castor VOMM) allowing for excellent solvent and impact resistance characteristics without any analogous detriment to flexibility. Castor VOMM thiol-ene films are therefore

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particularly suited for flexible thin film applications such as coil, optical fiber, and paper coatings.

**Summary**

Novel castor VOMMs were synthesized with acrylate, vinyl ether, and allyl ether functionalities. Each bio-based monomer exhibited excellent thin film performance in UV curable thiol-ene formulations. High solvent resistance and hardness along with excellent adhesion and flexibility were consistently achieved regardless of VOMM functionality. The final films contained approximately 40% vegetable oil on a weight basis without VOCs (systems formulated with driers contained minute levels of mineral spirits). Testing on films immediately upon cure and a week after UV exposure showed increased crosslinking and improved physical properties upon aging and a “dark cure” process.

FTIR spectroscopy was used to distinguish between homopolymerization and thiol-ene mechanisms. Vinyl ether groups copolymerized with cis-unsaturation in addition to thiol-ene polymerization. Thiol groups reacted with cis-unsaturation and allyl ethers. Acrylic double bonds underwent significant homopolymerization in addition to thiol-ene polymerization. Cis-unsaturation behaved differently in each of these systems but was always involved in initial curing and contributed to postcuring reactions.
References:


14) Snider, B.B.; Rodini, D.J.; Conn, R.S.E.; Sealfon, S. *Journal of the American Chemical Society*, **1979**, 5283-5293.


17) Smith, B. *Infrared Spectral Interpretation*, CRC Press, New York, **1999**.


CHAPTER V
CATIONIC PHOTOPOLYMERIZATION OF EPOXIDIZED SOYBEAN OIL

Introduction

Bio-based raw material utilization combined with the desire to decrease volatile organic compound (VOC) emissions from decorative and protective coatings are the two primary drivers for the research described herein. Current euphoric logic defines the perfect coating as one composed of renewable raw materials, that is applied with ease in the absence of volatile emissions, while providing toughness and durability normally only associated with thermosetting chemistries and maintaining unlimited storage stability. Decreasing VOC emissions from coatings remains an important endeavor because of environmental and health concerns. Photoinitiated polymerization processes rapidly convert low viscosity liquids to protective and decorative films with low/no VOC release, minimal heating requirements, and rapid curing as stated in earlier chapters.\textsuperscript{1,2} Polymers, oligomers, and reactive diluents utilized in photoinitiated free-radical polymerization are typically acrylates and methacrylates, as they polymerize quickly, and contain an ester group that is a convenient site for functionalization.\textsuperscript{3} In fact, several of the prepolymers and reactive diluents used in chapter 4 were acrylate functional materials. Unfortunately a balance must be met; low molecular weight monomers are relatively volatile, may have unpleasant odors, and commonly present potential health hazards.\textsuperscript{3} In addition, free-radical photopolymerization is inhibited by atmospheric oxygen,\textsuperscript{4} and curing in an inert atmosphere is not always practical. Cationic UV polymerization is an alternative
chemistry that is especially useful when immediate cure responses are not required.\textsuperscript{5}

Free-radical photopolymerizations are by far the most utilized radiation cured processes. Nevertheless, cationic photopolymerization offers unique advantages. Photoinitiated cationic polymerizations exhibit living polymerization characteristics\textsuperscript{6} and often continue polymerizing in the “dark” after being removed from the illumination source.\textsuperscript{7-9} Here the functional groups continue to react due to the presence of long-lived cations. The “dark” cure phenomenon is illustrated in Figure 5-1 for the UV induced cationic polymerization of tetrahydrofuran (THF).\textsuperscript{10} Photo-cationically cured epoxies exhibit relatively low shrinkage\textsuperscript{6}, increased adhesion, low vapor pressures, low viscosities, negligible toxicity, excellent clarity, and good abrasion and chemical resistance.\textsuperscript{4} Any protic nucleophile can cause chain-transfer to occur in cationic systems. Since water is an excellent chain-transfer agent, high humidity levels inhibit cationically cured systems and result in low functional group conversion and poor physical properties.\textsuperscript{9,11} Moreover, differences in relative humidity between locations will result in varying degrees of cure. Cationic photopolymerization is effective for a large variety of ring and vinyl ether monomers (Table 5-1). The ring structures all contain either oxygen or sulfur heteroatoms.
Figure 5-1. "Dark" reaction of the cationic photopolymerization of THF.\textsuperscript{10}

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<table>
<thead>
<tr>
<th>Name</th>
<th>Monomer Structure</th>
<th>Polymer Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Epoxide</td>
<td><img src="image" alt="Epoxide Structure" /></td>
<td><img src="image" alt="Epoxide Polymer Structure" /></td>
</tr>
<tr>
<td>Sulfoxide</td>
<td><img src="image" alt="Sulfoxide Structure" /></td>
<td><img src="image" alt="Sulfoxide Polymer Structure" /></td>
</tr>
<tr>
<td>1-Cycloxybutane</td>
<td><img src="image" alt="1-Cycloxybutane Structure" /></td>
<td><img src="image" alt="1-Cycloxybutane Polymer Structure" /></td>
</tr>
<tr>
<td>Tetrahydrofuran</td>
<td><img src="image" alt="Tetrahydrofuran Structure" /></td>
<td><img src="image" alt="Tetrahydrofuran Polymer Structure" /></td>
</tr>
<tr>
<td>Trioxane</td>
<td><img src="image" alt="Trioxane Structure" /></td>
<td><img src="image" alt="Trioxane Polymer Structure" /></td>
</tr>
<tr>
<td>Spirolactone</td>
<td><img src="image" alt="Spirolactone Structure" /></td>
<td><img src="image" alt="Spirolactone Polymer Structure" /></td>
</tr>
<tr>
<td>ε-Caprolactone</td>
<td><img src="image" alt="ε-Caprolactone Structure" /></td>
<td><img src="image" alt="ε-Caprolactone Polymer Structure" /></td>
</tr>
<tr>
<td>Cyclosiloxane</td>
<td><img src="image" alt="Cyclosiloxane Structure" /></td>
<td><img src="image" alt="Cyclosiloxane Polymer Structure" /></td>
</tr>
<tr>
<td>Vinyl ether</td>
<td><img src="image" alt="Vinyl Ether Structure" /></td>
<td><img src="image" alt="Vinyl Ether Polymer Structure" /></td>
</tr>
</tbody>
</table>

Renewable resource utilization is increasingly desirable in order to reduce petroleum feedstock dependency. Vegetable oil derivatives that have been
investigated in cationic UV polymerization for coatings and inks$^{12-14}$ include epoxidized linseed oil, epoxidized cycloaliphatic linseed oil, epoxidized castor oil, and epoxidized soybean oil.$^{7,15-18}$ Epoxidized soybean oil (ESO) results in improved UV resistance, corrosion resistance,$^7$ impact resistance, flexibility, and adhesion at the expense of film hardness.$^{17}$

Cationic photopolymerization is a chain-growth addition reaction initiated by very strong Brönsted acids. In epoxides, initiation occurs upon acid protonation of the epoxy oxygen, making the carbon alpha to the oxygen more electropositive. Polymerization propagates via reaction of unprotonated epoxides with the active carbons until chain-transfer with a nucleophile such as water terminates the process (Figure 5-2). Oxygen does not inhibit cationic polymerization, as oxygen exists as a triplet diradical.
Figure 5-2. Cationic polymerization of epoxides.

Photoinitiator Cation and Radical Formation

Crivello has been the most active in developing photoinitiators for cationic photopolymerization. The cationic photoinitiator forms cations, either directly or indirectly, through a sensitizer. Cationic photoinitiators are broadly classified as either ionic (e.g., onium and organometallic salts) and non-ionic (e.g., organosilanes and latent sulphonylic acids). Of these, onium salts, especially
diaryliodonium and triarylsulphonium salts, have enjoyed the most usage (Table 5-2).\textsuperscript{10} The non-nucleophilic anions, i.e., BF\textsubscript{4}\textsuperscript{-}, PF\textsubscript{6}\textsuperscript{-}, AsF\textsubscript{6}\textsuperscript{-}, and SbF\textsubscript{6}\textsuperscript{-}, are weak conjugate bases which yield super-acids.\textsuperscript{19}

**Table 5-2. Onium Salt Photoinitiators\textsuperscript{10}**

<table>
<thead>
<tr>
<th>General Name</th>
<th>Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aryldiazonium salts</td>
<td>(\text{Ar} - \text{N} = \text{N} ; \text{X}^\ominus)</td>
</tr>
<tr>
<td>Diaryliodonium salts</td>
<td>(\text{Ar}_2 - \text{I}^\ominus ; \text{X}^\ominus)</td>
</tr>
<tr>
<td>Triarylsulphonium salts</td>
<td>(\text{Ar}_3 - \text{S}^\ominus ; \text{X}^\ominus)</td>
</tr>
<tr>
<td>Triacrylselenonium salts</td>
<td>(\text{Ar}_3 - \text{Se}^\ominus ; \text{X}^\ominus)</td>
</tr>
<tr>
<td>Dialkylphenacylsulphonium salts</td>
<td>(\text{Ar} - \text{C} - \text{CH}_2 - \text{S} - \text{R}_2)</td>
</tr>
<tr>
<td>Triarylsulphoxonium salts</td>
<td>(\text{Ar}_3 - \text{S}^\ominus ; \text{X}^\ominus)</td>
</tr>
<tr>
<td>Aryloxydiarylsulphoxonium salts</td>
<td>(\text{Ar} - \text{O} - \text{S} - \text{Ar}_2)</td>
</tr>
<tr>
<td>Dialkylphenacylsulphoxonium salts</td>
<td>(\text{Ar} - \text{C} - \text{CH}_2 - \text{S} - \text{R}_2)</td>
</tr>
</tbody>
</table>

\(\text{X} = \text{counterion, Ar = aryl group, R = alkyl group}\)

The mechanism for the photodecomposition of triarylsulphonium salts and subsequent acid formation involves both homolytic and heterolytic reactions.\textsuperscript{4,20,21}

Figure 5-3 shows possible reaction pathways for generating the initiating acid.\textsuperscript{10}
Figure 5-3. Photochemical decomposition of a triarylsulphonium salt.

The presence of benzene and alkylbenzenes in the decomposition products is evidence for both homolytic and heterolytic cleavage. The hydrogen donor source can be any compound in the system with labile hydrogen atoms, such as...
allylic hydrogen atoms in vegetable oils. The remaining allylic radical then undergoes free-radical chain growth reaction. This study investigates the use of sulfonium cationic photoinitiators to mimic/accelerate auto-oxidation in partially epoxidized soybean oil. The primary goal of the project is to understand how unsaturation affects the complex curing behavior of partially epoxidized soybean oil.

**ESO Synthesis and Characterization**

ESO was prepared using the Prilezhaev reaction (Figure 5-4).\textsuperscript{22} 3-chloroperoxybenzoic acid (3-CPBA) is reacted with soybean oil in various ratios to form epoxidized and partially epoxidized materials.\textsuperscript{23} Fully epoxidized soybean oil is obtained by using a slight excess of 3-CPBA with soybean oil unsaturation, i.e., 6 equivalents of 3-CPBA for 1 equivalent of soybean oil.

![Figure 5-4. Soybean oil epoxidation reaction mechanism.](image)
3-CPBA was purified prior to reaction by dissolving in methylene chloride, removing the insoluble top layer by gravity filtration, and isolating the pure peracid by removing methylene chloride in vacuo. 25 g (0.028 mole) of soybean oil was dissolved in 25 mL of acetone in a three-neck, 250 mL round-bottom flask. The flask was cooled to approximately 0°C using an ice bath. 3-CPBA was dissolved in acetone and added dropwise to the flask via an addition funnel. Acetone was removed in vacuo upon complete addition of 3-CPBA. The resulting epoxidized soybean oil was dissolved in 100 mL of hexane, vacuum filtered, and passed through an aluminum oxide packed chromatography column to remove polar impurities such as residual 3-chlorobenzoic acid. Hexane was removed in vacuo to yield the epoxidized oil (Table 5-3).

Table 5-3. ESO Reactant Summary

<table>
<thead>
<tr>
<th>% Epoxidized</th>
<th>3-CPBA Mass (g)</th>
<th>Moles</th>
<th>Equivalents to SBO</th>
</tr>
</thead>
<tbody>
<tr>
<td>6 %</td>
<td>2.03</td>
<td>0.0118</td>
<td>0.42</td>
</tr>
<tr>
<td>14 %</td>
<td>5.07</td>
<td>0.0294</td>
<td>1.05</td>
</tr>
<tr>
<td>28 %</td>
<td>10.15</td>
<td>0.0588</td>
<td>2.10</td>
</tr>
<tr>
<td>41 %</td>
<td>15.22</td>
<td>0.0882</td>
<td>3.15</td>
</tr>
<tr>
<td>75 %</td>
<td>21.74</td>
<td>0.1260</td>
<td>4.50</td>
</tr>
<tr>
<td>82 %</td>
<td>24.16</td>
<td>0.1400</td>
<td>5.00</td>
</tr>
<tr>
<td>100 %</td>
<td>28.99</td>
<td>0.1680</td>
<td>6.00</td>
</tr>
</tbody>
</table>

$^1$H NMR spectroscopy was used to determine the percentage of epoxidation. Integration of the glycerol methylene protons (4.2 ppm, 4 protons) was compared to the residual vinylic protons (5.2 ppm). One proton (the glycerol methine) was subtracted in the calculation. The proton value for each sample was divided by the proton value for virgin soybean oil (approximately 10 protons) to obtain the percent unsaturation lost to epoxidation, i.e., the percent
epoxidized. The $^1$H NMR spectra for soybean oil, commercial ESO, and ESO synthesized for this study are provided in Figures 5-5 to 5-13.

Figure 5-5. $^1$H NMR spectrum of soybean oil.

Figure 5-6. $^1$H NMR spectrum of commercial ESO.
Figure 5-7. $^1H$ NMR spectrum of 6% ESO.

Figure 5-8. $^1H$ NMR spectrum of 14% ESO.

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Figure 5-9. $^1$H NMR spectrum of 28% ESO.

Figure 5-10. $^1$H NMR spectrum of 41% ESO.
Figure 5-11. $^1$H NMR spectrum of 75% ESO.

Figure 5-12. $^1$H NMR spectrum of 82% ESO.

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Moreover, the ESO was fully characterized by APT NMR spectroscopy. The APT NMR spectra for soybean oil, commercial ESO, and the ESO synthesized for this study are provided in Figures 5-14 to 5-22.
Figure 5-14. APT NMR spectrum of soybean oil.

Figure 5-15. APT NMR spectrum of commercial ESO.
Figure 5-16. APT NMR spectrum of 6% ESO.

Figure 5-17. APT NMR spectrum of 14% ESO.
Figure 5-18. APT NMR spectrum of 28% ESO.

Figure 5-19. APT NMR spectrum of 41% ESO.
Figure 5-20. APT NMR spectrum of 75% ESO.

Figure 5-21. APT NMR spectrum of 82% ESO.
Figure 5-22. APT NMR spectrum of 100% ESO.

GPC was to characterize the molecular weight distribution of ESO. Coconut oil was used as a standard as it does not body over time. Each of the ESO samples, regardless of degree of epoxidation, had molecular weights of approximately 900 g/mol (based on polystyrene standards). The combined GPC traces are shown in Figure 5-23, with the number average molecular weights ($M_n$) and polydispersity indices (PDIs) are listed in Table 5-4. Note that the shift towards higher molecular weight represents the addition of oxygen to the molecule as well as an increase solubility in THF for epoxidized oil.
Figure 5-23. GPC traces of epoxidized soybean oil compared to coconut oil standard.

Table 5-4. Mw and PDI of Epoxidized Soybean Oil.

<table>
<thead>
<tr>
<th>Sample</th>
<th>M_n (g/mol)</th>
<th>PDI</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO standard</td>
<td>682</td>
<td>1.06</td>
</tr>
<tr>
<td>6% ESO</td>
<td>922</td>
<td>1.04</td>
</tr>
<tr>
<td>14% ESO</td>
<td>917</td>
<td>1.05</td>
</tr>
<tr>
<td>28% ESO</td>
<td>906</td>
<td>1.05</td>
</tr>
<tr>
<td>41% ESO</td>
<td>911</td>
<td>1.05</td>
</tr>
<tr>
<td>75% ESO</td>
<td>897</td>
<td>1.05</td>
</tr>
<tr>
<td>82% ESO</td>
<td>904</td>
<td>1.05</td>
</tr>
<tr>
<td>100% ESO</td>
<td>901</td>
<td>1.05</td>
</tr>
</tbody>
</table>

ESO UV Cationic Formulation

All the ESO samples were blended with 2 phr UVI-6974 (Figure 5-24) and mixed at 1500 rpm for 1 minute prior to reaction. The formulations had very low
viscosities (Table 5-5) that increased with the epoxidation level. Samples for DMA and FTIR spectroscopy were cured by passing them 10 times through a Fusion UV conveyor line. Only the fully epoxidized samples exhibited initial cure characteristics, such as solidification upon exposure. Other formulations cured slowly in the weeks following the irradiation. Cationically curable thin film formulations were also applied to salt plates and cured using the Fusion UV conveyor to quantify the degree of unsaturation lost over a time period of two weeks.

![Figure 5-24. UVI-6974 photoinitiator structure.](image)

Table 5-5. Viscosity of ESO Formulations

<table>
<thead>
<tr>
<th>% Epoxidation</th>
<th>6</th>
<th>14</th>
<th>28</th>
<th>41</th>
<th>75</th>
<th>81</th>
<th>100</th>
</tr>
</thead>
<tbody>
<tr>
<td>Viscosity (P)</td>
<td>0.51</td>
<td>0.63</td>
<td>0.72</td>
<td>0.85</td>
<td>1.66</td>
<td>1.68</td>
<td>2.07</td>
</tr>
</tbody>
</table>

Initial Cure Profile Using RTIR Spectroscopy

The epoxy peak (830 cm⁻¹, C-O-C symmetric stretch)²⁴ confirmed the instantaneous conversion for cationic photopolymerization of ESO formulations. Figure 5-25 shows that the incomplete epoxy functional group conversion was evident for all formulations. The percent conversion for 6% and 14% ESO samples are not shown in Figure 5-25, as the peak used to monitor reaction was...
too small to accurately measure the degree of conversion. However, the epoxy groups in formulations cured on salt plates were completely consumed. This difference in extent of conversion is related to the disparity in light intensity between the Fusion UV conveyor (3 Watt/cm²) and RTIR (187 milliWatt/cm²).

![Graph showing initial functional group conversions](image)

**Figure 5-25.** ESO initial functional group conversions.

**Postcure Analysis via FTIR Spectroscopy**

Each formulation was tested according to three different scenarios, i.e., UV cure with two-week postcure in air, UV cure with two-week postcure in nitrogen, and no UV cure with two-week ambient drying. The cis-unsaturation peak at 3010 cm⁻¹ decreased over the course of two weeks in the ambient cured systems. In addition, the appearance of a peak at 3400 cm⁻¹ indicates
hydroperoxide formation. The changes in these two peaks are attributed directly to auto-oxidation. Very little cis-unsaturation was consumed during UV irradiation for the photopolymerized samples. Free radicals formed during photoinitiator decomposition can either abstract allylic radicals or combine with oxygen dissolved in the coating to form low energy aryl and alkyl peroxy radicals. Reaction with oxygen is more energetically favorable, since it is only diffusion limited. The rapid abstraction of allylic hydrogen atoms combined with the inherently low reactivity of internal double bonds preserve cis-unsaturation throughout the cationic photocuring process. The FTIR spectra for the ambient and UV cured samples are provided in Figures 5-26 to 5-35. 100% ESO is not shown as it contains no cis-unsaturation for detection; 82% ESO is not shown as its degree of unsaturation is below the FTIR detection limits.

![FTIR spectra](image)

**Figure 5-26.** 6% ESO ambient cure FTIR spectra.

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Figure 5-27. 6% ESO UV cure FTIR spectra.

Figure 5-28. 14% ESO ambient cure FTIR spectra.
Figure 5-29. 14% ESO UV cure FTIR spectra.

Figure 5-30. 28% ESO ambient cure FTIR spectra.
Figure 5-31. 28% ESO UV cure FTIR spectra.

Figure 5-32. 41% ESO ambient cure FTIR spectra.
Figure 5-33. 41% ESO UV cure FTIR spectra.

Figure 5-34. 75% ESO ambient cure FTIR spectra.
The formulations were also cured and tested in an inert environment. Both ambient and force cured samples were placed in a nitrogen box for 2 weeks and tested periodically using FTIR spectroscopy. The FTIR spectra for the 6% ESO ambient and UV cured samples postcured in nitrogen are provided in Figures 5-36 and 5-37. This data shows both curing conditions resulted in no consumption of internal unsaturation. All other ESO samples showed similar results. This suggests the lifetimes of the radicals produced by the cationic photoinitiator are short and the oxygen dissolved in the coating and/or antioxidants reacts quickly with the photoinitiator’s radicals.
Figure 5-36. Nitrogen purged 6% ESO ambient cure FTIR spectra.

Figure 5-37. Nitrogen purged 6% ESO UV cure FTIR spectra.

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DMA Analysis

Only the 100% epoxidized soybean oil produced a tractable film (storage modulus of 32 MPa at 75°C for 2 week aged sample). Figure 5-38 shows the DMA plot for fully epoxidized soybean oil. The other samples either did not form films or yielded films lacking the mechanical strength for testing, even after two weeks of postcure.

![DMA plot of 100% ESO aged for 2 weeks.](image)

Summary

Soybean oil was successfully epoxidized to various levels ranging from 6% to 100%. ESO blends with UVI-6974 produced low viscosity coatings that cured slowly when irradiated. Only the 100% ESO formed a film with sufficient mechanical strength for DMA analysis.
FTIR analysis confirmed that the epoxides reacted fully when irradiated with high intensity light and cured only partially when irradiated with low intensity light. The soybean oil cis-unsaturation was not consumed during photocure; this was attributed to the radical combination with molecular oxygen dissolved in the coating and/or anti-oxidants. Formation of alkyl- and arylperoxides is energetically favored over hydrogen abstraction.

The cis-unsaturation was consumed over the course of two weeks of "dark" cure in the ambient and UV-cured samples. This reaction cannot be accelerated by cationic photoinitiator free-radical decomposition products, because oxygen preferentially deactivates the radicals before they can abstract allylic hydrogen atoms on partially epoxidized soybean oil. Allylic hydrogen abstraction occurs only if the system was devoid of oxygen. However, oxygen removal is seldom performed commercially due to practical challenges, such as cost.
References:

CHAPTER VI

CHAIN TRANSFER TO VOMMS DURING FREE RADICAL POLYMERIZATION

History of VOMMs in Emulsion Polymerization

Using VOMMs for UV curable coatings is a relatively new endeavor for our research group. Traditionally, the emphasis was on using VOMMs in emulsion polymerizations as a means of incorporating auto-oxidizable alkyd materials while increasing the biobased raw materials content and utilization. Numerous VOMMs have been synthesized in our labs that promote coalescence during latex film formation and enhance film properties via auto-oxidative crosslinking. The earliest reference to VOMMs is noted in the synthesis and incorporation of acrylate functional fatty acids by reaction of fatty alcohols with acrylol chloride (Figure 6-1).8

![Figure 6-1. Acrylate functional fatty alcohol synthesis.](image)

In the early 1990s, acrylated castor oil methyl ester (CAM-I) was synthesized by transesterifying castor oil with methanol and subsequently esterifying the ricinoleic methyl esters with acrylic acid (Figure 6-2).9

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Copolymerization of CAM-I with conventional comonomers via emulsion polymerization exhibited low conversions at concentrations above 15 wt%\textsuperscript{10,11}

![Chemical structure of CAM-I](image)

**Figure 6-2. CAM-I synthesis.**

Acrylated castor oil (CAM-II) was also evaluated as a VOMM. CAM-II is more economical than CAM-I, as its synthesis involves the direct esterification of castor oil with acrylic acid (Figure 6-3).\textsuperscript{9} However, the hydrophobicity of CAM-II prevented its homogeneous incorporation into latexes.

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Synthesis of urethane VOMMs was initiated with the development of urethane castor acrylate monomer (UCAM). The urethane monomers improved the hydrolytic stability and hydrophilicity of VOMMs while enhancing the physical properties of the dried film via hydrogen bonding interactions. UCAM was synthesized by reacting castor oil with isophorone diisocyanate followed by 2-hydroxyethyl acrylate (Figure 6-4). These UCAM monomers created various problems when incorporated into emulsion polymers such as formation of insoluble coagulum.
Hydrophilic VOMMs were synthesized using soybean acrylate monomer (SAM). SAM was synthesized by reacting soybean oil with maleic anhydride through the ene reaction followed by esterification of the succinic anhydride moieties (Figure 6-5). The resulting SAM carboxylic acids were neutralized to various levels to enhance its hydrophilicity and aid VOMM diffusion through the aqueous phase. However, the increased hydrophilicity resulted in undesirable levels of water sensitivity in the final film.
Figure 6-5. SAM synthesis.

Soybean amide acrylate (Soy AA-1) was synthesized by the amidation of soybean oil with 2-(methylamino) ethanol followed by esterification with acryloyl...
chloride (Figure 6-6). Soy AA-1 is lower in molecular weight than other VOMMs and combines sufficient hydrophilicity with good hydrolytic stability. In addition, it can be reproducibly synthesized at high purity.

![Figure 6-6. Soy AA-1 synthesis.](image)

To date, Soy AA-1 appears to be the best candidate for emulsion polymerization as it is readily incorporated into the latex particles. While exhaustive testing of Soy AA-1 latexes has not been carried out to completion, it has been shown to successfully reduce the MFT of coatings through plasticization, and raise the $T_g$ after application via auto-oxidative polymerization. What is not known with any of the VOMMs shown above is the maximum amount of $T_g$ reduction and gain for emulsions formulated with them. Part of the reason for our lack of understanding is due to side reactions during the emulsion polymerization of VOMMs with comonomers, which create gel fractions, reduce polymer molecular weight, and possibly reduce auto-oxidation potential.
**Typical Side Reactions During Polymerization**

VOMMs are designed to copolymerize with conventional acrylic monomers during emulsion polymerization and utilize the unsaturation to build film properties via auto-oxidation after initial application. This process, however, is complicated by chain transfer between VOMMs and initiator/polymer radicals. Besides reducing the latex molecular weight, chain transfer reactions also reduce the allylic hydrogen content, and reduce the overall potential for auto-oxidation for final coating performance. Chain transfer is observed in all free radical polymerizations including bulk, solution, and emulsion polymerizations. This is also true of polymerizations performed in the presence of unsaturated vegetable oils. Diamond showed using photo-differential scanning calorimetry that the maximum polymerization rate of hexanediol diacrylate decreases when polymerized in the presence of unsaturated oils. As a model study for this research, solution polymerizations were performed to control the heat liberated during polymerization and provide maximum material species quantification throughout the reaction. The research goal was to determine the extent and location of chain transfer that occurs when acrylic monomers (methyl methacrylate and butyl acrylate) are copolymerized in the presence of vegetable oils and vegetable oil derivatives. Acrylate conversion was measured as a function of time via *in situ* FTIR spectroscopy.

**In Situ FTIR Analysis During Polymerization Processes**

Chain transfer was quantified from monomer conversion by observing the (meth)acrylate double bond peak (810 cm\(^{-1}\), C-H bend). Copolymerizations
involving vegetable oils and their derivatives exhibited retardation in the polymerization rate and a decrease in monomer conversion at time, t. Figure 6-7 is a representative IR spectrum, while Figure 6-8 displays a typical waterfall plot for the control polymerization.

Figure 6-7. FTIR spectrum highlighting the acrylate peak of the control polymerization.

Figure 6-8. 3D spectrum waterfall plot of acrylate peak (810 cm\(^{-1}\)) of the control polymerization over 5 hours.
Control polymers were synthesized in the absence of VOMMs. 20.81 g (0.162 mole) of butyl acrylate, 15.82 g (0.158 mole) of methyl methacrylate, and 160 mL of benzene were added to a 250 mL, three-neck, round bottom flask. The flask was equipped with a magnetic stir bar, a reflux column, a thermocouple and temperature probe, and a DiComp™ ATR probe. The monomer solution was heated to 75°C using a J-KEM® Gemini temperature control unit. Recrystallized AIBN was added (0.6 g, 3.6 mmole) to the reaction flask and data collection was initiated once the temperature reached 75°C. Experimental copolymerizations were conducted by incorporating 9-33 wt% (based on total monomer weight) of vegetable oil and vegetable oil derivatives to the original control formulation. The molar ratios of fatty acids, ethoxylated fatty alcohols, and triglycerides to monomer for the given weight percentages are listed in table 6-1.

<table>
<thead>
<tr>
<th>Weight Percent</th>
<th>Monomer: Fatty acid</th>
<th>Monomer:Ethoxylated Fatty Alcohol</th>
<th>Monomer:Triglyceride</th>
</tr>
</thead>
<tbody>
<tr>
<td>9%</td>
<td>25:1</td>
<td>43:1</td>
<td>80:1</td>
</tr>
<tr>
<td>17%</td>
<td>12:1</td>
<td>22:1</td>
<td>40:1</td>
</tr>
<tr>
<td>23%</td>
<td>8:1</td>
<td>14:1</td>
<td>26:1</td>
</tr>
<tr>
<td>29%</td>
<td>6:1</td>
<td>11:1</td>
<td>21:1</td>
</tr>
<tr>
<td>33%</td>
<td>5:1</td>
<td>9:1</td>
<td>17:1</td>
</tr>
</tbody>
</table>

Copolymerizations in the presence of stearic acid were studied first to validate the experimental method, since it was not expected to participate in chain transfer reactions. Monomer conversions for polymerizations containing 9-33 wt% stearic acid are shown in Figure 6-9. As expected, no difference was noted between the control and the reactions containing stearic acid.
Figure 6-9. Acrylate functional group conversion for polymerizations conducted in the presence of stearic acid.

Copolymerizations performed in the presence of oleic acid exhibited reduced monomer conversion and decreasing polymerization rates with increasing oleic acid concentration (Figure 6-10). The onset of degradative chain transfer is noted 2 hours into the reaction. Oleic acid has a single double bond at the 9th carbon atom. The most likely source of chain transfer is through the abstraction of an allylic hydrogen atom by a growing polymer chain or initiator fragment. The resulting radical is situated alpha to the double bond and is resonance stabilized. The allylic radical on the fatty acid chain also reacts with growing polymer chains or initiator fragments via bimolecular coupling, as this is only a diffusion limited recombination process.
Several vegetable oil-based surfactants were also studied to quantify additional chain transfer potential reactions during emulsion polymerization. The first step was to quantify the kinetic effects of each in solution polymerization before attempting emulsion conditions. Chemonic® O-5 and Brij® 72 are ethoxylated derivatives of oleic acid and stearic acid, respectively (hereafter referred to as EO-5 and ES-5), with an average of five ethoxy groups per molecule. Solution polymerizations with EO-5 exhibited ReactIR profiles similar to those of oleic acid, i.e., monomer conversion decreased with increasing concentration, as shown in Figure 6-11. However, at the same level of incorporation, total monomer conversion in every EO-5 copolymerization was lower than with oleic acid. The lower conversion observed in EO-5...
copolymizations is attributed to chain transfer to hydroperoxide impurities within EO-5. For example, polyethers were shown by Chiantore and coworkers\textsuperscript{17} to increase hydroperoxide formation, which participate in and aid chain transfer reactions. Figure 6-12 shows the conversion plots for copolymerizations with increasing levels of ES-5. Acrylate comonomer conversion did not change with increasing ES-5 concentration, although ES-5 also contains hydroperoxides.

![Conversion plots for copolymerizations with increasing levels of ES-5.](image)

**Figure 6-11.** Acrylate functional group conversion for polymerizations conducted in the presence of EO-5.
Figure 6-12. Acrylate functional group conversion for polymerizations conducted in the presence of ES-5.

Surfactants with ethoxy units of varying molecular weights were also evaluated. Solution polymerizations conducted in the presence of polyethylene glycol (PEG 1000, molecular weight of approximately 1000 g/mol) exhibited only a slight variation, supportive of very little chain transfer (similar to stearic acid) (Figure 6-13). After much evaluation and discussion, these unexpected observations are best explained through longer wavelength infrared spectral analysis specific to EO-5, ES-5, and PEG 1000.
Results of detailed analysis of the hydroperoxide vibrations (3300-3450 cm\(^{-1}\)) are summarized in Figures 6-14 to 6-16 through waterfall plots. Spectra from reactions containing EO-5 and PEG 1000 reveal that only negligible quantities of hydroperoxides are present initially (Figures 6-14 and 6-15, respectively). Polymerization in the presence of EO-5 is retarded primarily due to chain transfer with allylic hydrogen atoms of the oleic fatty acids. The absence of both abstractable allylic hydrogens and hydroperoxides in PEG 1000 minimizes its ability to retard polymerization even at high concentrations. In contrast, ES-5 possesses high initial hydroperoxide concentration (Figure 6-16) thought to be caused by ethylene oxide/or potentially other contaminants. Shown in Figure 16, the IR peak diminishes rapidly during the first hour of polymerization.
Figure 6-14. Waterfall plot of polymerization in the presence of 33% PEG 1000.

Figure 6-15. Waterfall plot of polymerization in the presence of 33% EO-5.
Figure 6-16. Waterfall plot of polymerization in the presence of 33% ES-5.

Higher concentrations of oleic acid and EO-5 reduced the polymerization rates and hinder monomer conversion in comparison with the control at the end of 5 hours. MMA and BA conversion plots for polymerizations in the presence of 33 wt% additives are shown in Figure 6-17.
Figure 6-17. Acrylate functional group conversion for polymerizations conducted in the presence of 33 wt% additives.

Chain transfer greatly retarded the polymerization rate in reactions conducted in the presence of vegetable oils with the effect increasing in order of soybean oil, linseed oil, and tung oil. Polymerization was almost completely inhibited in the presence of 33% tung oil. Tung oil contains approximately 70% α-eleostearic acid, a fatty acid with three conjugated double bonds and thus 4 highly resonance stabilized abstractable hydrogen atoms. Linseed oil contains approximately 60% linolenic acid (6 less abstractable hydrogen atoms than in eleostearic) and 14% linoleic acid with three and two double bonds, respectively (unconjugated in the natural state). Soybean oil contains 8% linolenic acid and
55% linoleic acid. Higher unsaturation (greater electron delocalization) increases the resonance stability and lifetime of the radical and promotes additional chain transfer reactions. The activation energy for hydroperoxide formation is lower in linolenic and linoleic fatty acids than in oleic acid due to the active methylene group between the double bonds.\textsuperscript{19} The bond dissociation energy for monoallylic hydrogen atoms is 86 kcal/mol and 10 kcal/mol less than that for bisallylic hydrogen atoms.\textsuperscript{20} Allylic radicals are even more easily stabilized by conjugated double bond systems.

The polymerizations were further analyzed in order to determine the allylic double bond ratio before and after acrylate copolymerization. The effect of free-radical polymerization on vegetable oil unsaturation was evaluated via solution polymerization of methyl methacrylate in benzene with and without soybean oil under the same previous reaction conditions. The soybean oil unsaturation (5.3 ppm) peak was integrated and compared to the glycidyl methylene protons (4.2 ppm) before and after polymerization (Figures 6-18 and 6-19). Soybean oil had approximately 8.4 double bond protons before the reaction and approximately 7.6 protons after polymerization. Since the margin of error associated with this technique is approximately 10%, it was inferred that most double bonds were retained after polymerization.
Figure 6-18. $^1$H NMR spectrum of soybean oil.

Figure 6-19. $^1$H NMR spectrum of PMMA after solution polymerization in the presence of 33% soybean oil.

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Mayo Analysis for Chain Transfer Constants

Mayo analysis was conducted to determine chain transfer constants using equation 6-1, where \( X_n \) is degree of polymerization, \( X_{n0} \) is degree of polymerization in the absence of externally added chain transfer agent, \( k_{ct} \) is the chain transfer constant, \( k_p \) is the propagation constant, \([S]\) is the chain transfer agent concentration, and \([M]\) is the monomer concentration.\(^{17,19,21}\)

\[
(1/X_n) = (1/X_{n0}) + (k_{ct}/k_p)([S]/[M])
\]

Equation 6-1. Mayo equation.

A monomer with known \( k_p \) value is polymerized in the presence of varying concentrations of chain transfer agent \((S)\). \( k_{ct} \) is calculated from the slope of \((1/X_n)\) plotted against \(([S]/[M])\) as shown in Figure 6-20.

\[
\frac{1}{X_n}
\]

\[
\frac{k_{ct}}{k_p}
\]

\[
\frac{1}{X_{n0}}\]

\[
[S]/[M]
\]

Figure 6-20. Mayo plot.

AlBN initiated bulk MMA \((k_p = 0.515 \times 10^3 \text{ l/mole*sec at 60°C})^{14}\) polymerizations were performed at 60°C and stopped at low conversion \((< 10\%)\). The polymerization was repeated in the presence of varying amounts of the chain transfer agent. MMA as received contains 25 ppm 4-
methoxyhydroquinone (4-MEHQ) and was passed through activated basic alumina (pore size 50-200 μ) to remove the inhibitor prior to polymerization. Gas chromatography confirmed the complete removal of 4-MEHQ.

Dodecanethiol was used to validate the experimental procedure. AIBN (0.08g, 0.0005mol) and purified MMA (5g, 0.05mole) were blended in a scintillation vial. Dodecanethiol was added at varying concentrations to identical AIBN/MMA solutions (Table 6-2). Nitrogen was bubbled through the solutions for 10 minutes. The vials were capped and stirred magnetically in an oil bath at 60°C for 5 minutes. A spatula tip amount of hydroquinone was added to each vial before transferring them to an ice bath to quench the polymerization.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Mass (g)</th>
<th>Moles</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>0.02</td>
<td>0.0001</td>
</tr>
<tr>
<td>3</td>
<td>0.04</td>
<td>0.0002</td>
</tr>
<tr>
<td>4</td>
<td>0.06</td>
<td>0.0003</td>
</tr>
<tr>
<td>5</td>
<td>0.08</td>
<td>0.0004</td>
</tr>
<tr>
<td>6</td>
<td>0.1</td>
<td>0.0005</td>
</tr>
</tbody>
</table>

GPC analysis was performed using PMMA standards. Table 6-3 summarizes the molecular weights (and corresponding Xn values) of the resulting polymers along with monomer and chain transfer agent concentrations for each reaction.
Table 6-3. Polymerization Data for MMA Polymerizations with Dodecanethiol

<table>
<thead>
<tr>
<th>Sample</th>
<th>( M_n ) (g/mol)</th>
<th>( X_n )</th>
<th>([M])</th>
<th>([S])</th>
<th>([S]/[M])</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>65,338</td>
<td>653</td>
<td>9.40</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>37,812</td>
<td>378</td>
<td>9.36</td>
<td>0.019</td>
<td>0.002</td>
</tr>
<tr>
<td>3</td>
<td>19,513</td>
<td>195</td>
<td>9.31</td>
<td>0.037</td>
<td>0.004</td>
</tr>
<tr>
<td>4</td>
<td>15,519</td>
<td>155</td>
<td>9.28</td>
<td>0.056</td>
<td>0.006</td>
</tr>
<tr>
<td>5</td>
<td>11,696</td>
<td>117</td>
<td>9.24</td>
<td>0.074</td>
<td>0.008</td>
</tr>
<tr>
<td>6</td>
<td>10,037</td>
<td>100</td>
<td>9.19</td>
<td>0.092</td>
<td>0.010</td>
</tr>
</tbody>
</table>

The Mayo plot for dodecanethiol (Figure 6-21) yielded a \( k_{ct} \) value of 450 l/mole*sec, consistent with values found in literature (ranges from 500 to 778 l/mole*sec).\(^{22}\) A duplicate experiment yielded a \( k_{ct} \) value of 438 l/mole*sec with an \( R^2 \) value of 0.998.

![Mayo plot for dodecanethiol](image.png)

Figure 6-21. Mayo plot for dodecanethiol.
The technique was repeated with soybean oil and linseed oil in place of dodecanethiol (Table 6-4). Table 6-5 provides the molecular weights (and corresponding $X_n$ values) of the resulting polymers.

**Table 6-4. Soybean Oil and Linseed Oil Concentrations**

<table>
<thead>
<tr>
<th>Mass (g)</th>
<th>mmoles</th>
<th>Mass (g)</th>
<th>mmoles</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>0.02</td>
<td>0.02</td>
<td>0.02</td>
<td>0.02</td>
</tr>
<tr>
<td>0.04</td>
<td>0.05</td>
<td>0.04</td>
<td>0.05</td>
</tr>
<tr>
<td>0.06</td>
<td>0.07</td>
<td>0.06</td>
<td>0.07</td>
</tr>
<tr>
<td>0.08</td>
<td>0.09</td>
<td>0.08</td>
<td>0.09</td>
</tr>
<tr>
<td>0.1</td>
<td>0.11</td>
<td>0.1</td>
<td>0.11</td>
</tr>
</tbody>
</table>

**Table 6-5. Polymerization Data for MMA Polymerizations with Soybean Oil and Linseed Oil**

<table>
<thead>
<tr>
<th>Soybean Oil</th>
<th>$M_n$ (g/mol)</th>
<th>$X_n$</th>
<th>Linseed Oil</th>
<th>$M_n$ (g/mol)</th>
<th>$X_n$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>53,484</td>
<td>535</td>
<td>1</td>
<td>52,749</td>
<td>528</td>
</tr>
<tr>
<td>2</td>
<td>54,883</td>
<td>549</td>
<td>2</td>
<td>62,992</td>
<td>630</td>
</tr>
<tr>
<td>3</td>
<td>54,877</td>
<td>549</td>
<td>3</td>
<td>49,240</td>
<td>492</td>
</tr>
<tr>
<td>4</td>
<td>54,564</td>
<td>546</td>
<td>4</td>
<td>48,166</td>
<td>482</td>
</tr>
<tr>
<td>5</td>
<td>58,875</td>
<td>589</td>
<td>5</td>
<td>48,876</td>
<td>489</td>
</tr>
<tr>
<td>6</td>
<td>62,100</td>
<td>621</td>
<td>6</td>
<td>51,663</td>
<td>517</td>
</tr>
</tbody>
</table>
The Mayo plots with the data for both soybean oil and linseed oil experiments did not exhibit the linear results required for the Mayo analysis. This could be attributed to the highly variable number of potential chain transfer locations and variability in fatty acid distribution. After an exhaustive literature search, no supportive data was found. Therefore, it was decided that the data should be included although it was not useful for our model experiments. Apparently, other researches have encountered similar issues with determining chain transfer constants for oils, since there are no recorded chain transfer constants for unsaturated oils. The *Polymer Handbook* reports combined chain transfer constants \( (C_s) \) for methyl oleate \((1.68 \times 10^{-4} \text{ and } 8.0 \times 10^{-4})\) and methyl stearate \((0.282 \times 10^{-4})\).

**Fluorescent Tagging and GPC Analysis for Chain Transfer Measurements**

MMA was polymerized in the presence of fluorescent tagged fatty acids to determine and simulate whether vegetable oils deliver hydrogen atoms and graft to polymer chains after chain transfer or simply act as a source of abstractable hydrogens. As radical coupling is essentially diffusion controlled, \((10^9 \text{ M}^{-1} \text{sec}^{-1})\), polymer radicals should combine with vegetable oil macromonomer allylic radicals. A GPC method was developed between our labs and Dr. Bob Gilbert’s Key Centre for Polymer Colloids at the University of Sydney, Australia. The method uses a refractive index (RI) detector in parallel with an ultraviolet (UV) detector. The basic idea behind these experiments is illustrated in Figure 6-22. The fluorescent tagged fatty acids are the only UV active material in the polymerizations. In scenario 1, if the fatty acids are ultimately covalently bound
to the polymer chains, either through initiation of MMA by allylic radicals or by termination of growing MMA chains by allylic radicals, then the UV and RI responses will overlap. In scenario 2, if the fluorescent tagged fatty acids do not become tethered to the polymer chains, then the UV and RI responses will not overlap and will elute separately, at longer times.

Figure 6-22. GPC of MMA polymerizations with UV and RI detector in parallel.

Stearic acid, oleic acid, linoleic acid, soybean oil fatty acids, and linseed oil fatty acids were fluorescent tagged with 1-aminopyrene. 1-Aminopyrene proved to be an ideal fluorophore for these experiments, as it has a strong absorbance at approximately 360 nm (Figure 6-23) and lies was within the detection limit of the GPC’s UV detector. The absorbance at 280 nm is due to THF. Oleic and stearic acid solutions in THF at concentrations 20 times greater than the 1-aminopyrene THF solutions were analyzed by UV-VIS spectroscopy. These fatty acids have no competitive absorbance to complicate analysis.
Figure 6-23. UV-VIS absorbance of 1-aminopyrene and oleic/stearic acid.

The fatty acids were fluorescent tagged through DCC coupling in THF (Figure 6-24). DCC coupling has been widely used to fluorescent tag chemicals. The products were characterized via $^{13}$C NMR spectroscopy. The carboxylic acid carbon (approximately 180 ppm) shifted to the amide carbon (approximately 174 ppm) in all the tagging reactions. Figure 6-25 shows the $^{13}$C NMR spectrum for oleic acid. The other fatty acids have the same carbonyl peak assignment as that of oleic acid.
Figure 6-24. DCC coupling reaction of fatty acids with 1-aminopyrene.

Figure 6-25. $^{13}$C NMR spectrum of oleic acid.
**Fluorescent Tagged Stearic Acid**

0.1376 g (0.5 mmole) stearic acid, 0.1 g (0.5 mmole) of DCC, and 0.1 g (0.5 mmole) of 1-aminopyrene were added to 10 mL of THF in a scintillation vial. The vial was shaken and allowed to stand for 3 days. The solution was passed through an aluminum oxide packed column to remove residual DCC and dicyclohexyl urea (DCU). THF was removed *in vacuo*. The $^{13}$C NMR spectrum for fluorescent tagged stearic acid is shown in Figure 6-26.

![Figure 6-26. $^{13}$C NMR spectrum of fluorescent tagged stearic acid.](image-url)

**Fluorescent Tagged Oleic Acid**

0.1367 g (0.5 mmole) of oleic acid, 0.1 g (0.5 mmole) of DCC, and 0.1 g (0.5 mmole) of 1-aminopyrene were added to 10 mL of THF in a scintillation vial. The vial was shaken and allowed to stand for 3 days. The solution was passed through an aluminum oxide packed column to remove residual DCC and DCU.
THF was removed \textit{in vacuo}. The $^{13}$C NMR spectrum for fluorescent tagged oleic acid is shown in Figure 6-27.

Figure 6-27. $^{13}$C NMR spectrum of fluorescent tagged oleic acid.

\textit{Fluorescent Tagged Linoleic Acid}

0.14 g (0.5 mmole) of linoleic acid, 0.1 g (0.5 mmole) of DCC, and 0.1 g (0.5 mmole) of 1-aminopyrene were added to 10 mL of THF in a scintillation vial. The vial was shaken and allowed to stand for 3 days. The solution was passed through an aluminum oxide packed column to remove residual DCC and DCU. THF was removed \textit{in vacuo}. The $^{13}$C NMR spectrum for fluorescent tagged linoleic acid is shown in Figure 6-28.
Figure 6-28. $^{13}$C NMR spectrum of fluorescent tagged linoleic acid.

**Fluorescent Tagged Soybean Oil Fatty Acids**

0.14 g (0.5 mmole) of soybean oil fatty acids, 0.1 g (0.5 mmole) of DCC, and 0.1 g (0.5 mmole) of 1-aminopyrene were added to 10 mL of THF in a scintillation vial. The vial was shaken and allowed to stand for 3 days. The solution was passed through an aluminum oxide packed column to remove residual DCC and DCU. THF was removed *in vacuo*. The $^{13}$C NMR spectrum for fluorescent tagged soybean oil fatty acid is shown in Figure 6-29.
Figure 6-29. $^{13}$C NMR spectrum of fluorescent tagged soybean fatty acids.

**Fluorescent Tagged Linseed Oil Fatty Acids**

0.14 g (0.5 mmole) of linseed oil fatty acids, 0.1 g (0.5 mmole) of DCC, and 0.1 g (0.5 mmole) of 1-aminopyrene were added to 10 mL of THF in a scintillation vial. The vial was shaken and allowed to stand for 3 days. The solution was passed through an aluminum oxide packed column to remove residual DCC and DCU. THF was removed *in vacuo*. The $^{13}$C NMR spectrum for fluorescent tagged linseed oil fatty acid is shown in Figure 6-30.
Figure 6-30. $^{13}$C NMR spectrum of fluorescent tagged linseed fatty acids.

**Bulk Polymerization of MMA**

MMA was polymerized in bulk to determine if the fatty acids provided abstractable hydrogen atoms or attached directly to polymer chains. MMA was purified by distillation to remove high molecular weight polymer and inhibitor, and AIBN was purified via recrystallization in methanol. Oxygen was removed from all polymerizations by three successive freeze-pump-thaw cycles. The bulk polymerizations were limited to low conversions (approximately 5%) to avoid auto-acceleration. Conversion was determined gravimetrically.

The control polymers were synthesized first. 5 g (0.0499 mole) of freshly distilled MMA was added along with 0.017 g (0.01 mmole) of AIBN to a Schlink flask. After three freeze-pump-thaw cycles, the flask was heated in an oil bath at 75°C for 10 minutes. The flask was transferred to quench the polymerization.
Hydroquinone was added. The percent conversion was determined to be 5.81%. Other controls were synthesized in like manner and their percent conversions ranged from 1.7 to 3.7%.

MMA was polymerized with 0.1 mol % of each fluorescent tagged fatty acid using the same reaction conditions as the control polymers. 5 g (0.0499 mole) MMA, 0.017 g (0.01 mmole) AIBN, and 0.024 g (0.005 mmole) of fluorescent tagged fatty acid were added to a Schlink flask. After three freeze-pump-thaw cycles, the flask was heated with an oil bath at 75°C for 10 minutes. The flask was transferred to an ice bath to quench the polymerization. Hydroquinone was added to each sample before GPC analysis. Fluorescent tagged stearic acid was used as a secondary control as it does not have chain transfer sites.

The GPC trace for the control is shown in Figure 6-31. The PMMA peak eluting at 20 minutes is monomodal and tails to higher elution times, indicating low molecular weight termination products. HQ elutes at 42.5 minutes and THF elutes at 44 minutes. The data range for the fluorescent tagged fatty acid polymerizations has been reduced to exclude HQ and THF elution times from the plots.
Figure 6-31. GPC trace for the control polymerization.

Figure 6-32 shows the UV detected GPC trace for fluorescent tagged oleic acid and stearic acid, labeled UVFTOA and UVFTSA, respectively, and the RI detected GPC trace for fluorescent tagged oleic acid and stearic acid, labeled RIFTOA and RIFTSA, respectively. The RI detector showed polymer peaks eluting at 20 minutes but the UV detector did not give a corresponding response. The absorbance beginning at 36 minutes, displayed with both the UV and RI detectors, is due to the fluorescent tagged fatty acids. These results indicated that both fatty acids did not bind covalently to the MMA polymer under these reaction conditions. Stearic acid has no chain transfer sites and the in situ IR studies showed that it did not affect the polymerization rate for free radical copolymerization of BA and MMA. However, FTIR studies indicated that
increasing amounts of oleic acid did indeed lower the polymerization rate. The rate did not appear to change until 1.5 hours into the solution polymerization. At low conversion, propagation appears to be more energetically favored than hydrogen abstraction.

![Figure 6-32. GPC trace for polymerizations in the presence of fluorescent tagged oleic and stearic acids.](image)

Figure 6-32 shows the UV detected GPC trace for fluorescent tagged linoleic acid, linseed oil fatty acids, and soybean oil fatty acids, labeled linoleicUV, linseedUV, and soyUV, respectively, and the RI detected GPC trace for fluorescent tagged linoleic acid, linseed oil fatty acids, and soybean oil fatty acids, labeled linoleicRI, linseedRI, and soyRI, respectively. Similar to the stearic and oleic acid experiments, the RI detector showed polymer peaks starting at 20 minutes elution time, with no corresponding response observed by the UV
detector. These results indicate that although these three fatty acids contain easily abstractable diallylic hydrogen atoms, they do not covalently bond to the MMA polymer under these reaction conditions. Reaction of radicals with surrounding monomer appears to be more energetically favorable than hydrogen abstraction.

Figure 6-33. GPC trace for polymerizations in the presence of fluorescent tagged linoleic, linseed oil, and soybean oil fatty acids.

Summary

VOMMs improve particle coalescence in emulsions, thereby reducing or eliminating the need for VOCs. In addition, these materials enhance film performance properties via auto-oxidative crosslinking. Even though chain transfer reactions with VOMMs reduce latex molecular weight and potentially the
auto-oxidation potential, the plasticization effect is clear and the reduced molecular weight is tolerable. Further study is needed to quantify the idealized limits for combined polymer, coating and film performance.

*In situ* IR studies showed that unsaturated fatty acids, fatty acid derivatives, and triglycerides reduce polymerization rate. Retardation in polymerization rate increases with the amount of unsaturation and conjugated unsaturation. Bisallylic hydrogen atoms, as found in linoleic and linolenic fatty acids, are more reactive than monoallylic hydrogen atoms due to their enhanced stability. Conjugated double bonds, as found in α-oleostearic acid (tung oil), completely inhibit polymerization. PEG, singularly, did not affect the polymerization rate. However, chain transfer can occur if hydroperoxides are present.

$^1$H NMR studies showed that MMA homopolymerization in the presence of soybean oil resulted in negligible loss of unsaturation in soybean oil. This indicated the growing polymer chains reacted primarily with allylic hydrogen atoms rather than adding to the double bond. GPC was employed to determine if the resulting allylic radicals reinitiate polymerization and/or couple with growing polymer chains. However, the experimental conditions did not facilitate coupling of tagged fatty acids with the polymer main chain. Coupling can occur at longer reaction times when less unreacted monomer is present, providing more opportunity for the relatively large vegetable oil structures to encounter polymer radicals.
References:

4) Thames, S.F.; Fruchey, O.; Panjnani, K. U.S. 6,174,948.
5) Thames, S.F.; Fruchey, O.; Panjnani, K. U.S. 6,599,972.
6) Thames, S.F.; Fruchey, O.; Panjnani, K. U.S. 6,001,913.
7) Thames, S.F.; Fruchey, O.; Panjnani, K. U.S. 6,897,255.
13) Unpublished results.
CHAPTER VII

MODEL FATTY ACID-FUNCTIONALIZED METHACRYLIC COPOLYMERS

Benchmark Polymers

As discussed in chapter 6, a technical challenge with VOMM incorporation in emulsion polymerization is the participation of allylic hydrogen atoms in chain transfer reactions through abstraction by propagating radicals. ¹ The quantifiable negative effects of chain transfer reactions include reduced rate of polymerization, shorter polymer kinetic chain length, and possibly a reduction in available unsaturation for auto-oxidation after film formation. The effects ultimately reduced performance properties compared to the ideal situation. ² In VOMMs, allylic hydrogen abstraction has been shown to be the primary mode of chain transfer, with the VOMM unsaturation playing a minimal role. ³ Steric hindrance surrounding the VOMM internal unsaturation promotes chain transfer via allylic hydrogen abstraction as the more energetically favored and accessible reaction pathway. ¹ Resonance stabilization of the resulting allylic radical lowers the potential for main chain copolymerization, albeit possibly a great termination site. VOMMs with higher unsaturation, especially conjugated unsaturation, increase the number of chain transfer events, as detected by reduced molecular weight. ³

It is important to preserve the VOMM unsaturation through the emulsion process to validate improved performance characteristics after application. ⁴ Complete inhibition of all chain transfer events would ideally quantify the limits of performance obtainable with a given VOMM copolymer for both film plasticization
and autooxidation. The research described below was an attempt to investigate and quantify such a benchmark. Copolymers employing methyl methacrylate (MMA), butyl acrylate (BA), and hydroxyethyl methacrylate (HEMA) were synthesized via free radical polymerization. The 1° hydroxyl groups of these copolymers were subsequently reacted with fatty acids, and resulting materials used auto-oxidation and gel content studies to establish baseline physical characteristics for VOMM-based acrylic copolymers formed in the absence of chain transfer.

**Fatty Acid-Grafted Polymer Synthesis and Characterization**

The synthetic method for attaching fatty acids to the acrylic polymer had to be mild enough to ensure that chain transfer reactions were undetectable in quantity. Dicyclohexylcarbodiimide (DCC) coupling provides for ester synthesis via the dehydration of carboxylic acids and alcohols with dicyclohexylurea (DCU) formed as the byproduct. The reaction scheme for DCC coupling of a carboxylic acid with an alcohol is shown in Figure 7-1.5

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The synthetic scheme for the fatty acid functionalized meth(acrylic) polymer is shown in Figure 7-2. The meth(acrylic) polymers were synthesized first via solution copolymerization. The HEMA proportion was varied to yield a range of functional polymers for each fatty acid. Fatty acids were reacted with equimolar amounts of DCC before reacting with the HEMA copolymer.
Figure 7-2. Synthesis of fatty acid functionalized methacrylic polymers.

Fatty acids were varied to give a range of copolymers with variable drying capability. Stearic acid copolymers serve as the controls, as they are completely saturated and have no potential for auto-oxidation. This is verified by the $^{13}$C NMR spectrum for stearic acid which shows no vinylic carbons (figure 7-3).

Figure 7-3. $^{13}$C NMR spectrum for stearic acid.
Figure 7-4 shows the $^{13}$C NMR spectrum for oleic acid. Oleic acid has one double bond at the 9th carbon position. Integration of the $^1$H NMR spectrum for oleic acid confirmed the presence of 1 double bond per fatty acid.

Soybean oil fatty acids contain approximately 15% saturated, 22% oleic, 55% linoleic, and 8% linolenic fatty acids. Integration of the $^1$H NMR spectrum for soybean oil fatty acids yields 1.5 double bonds per fatty acid. The higher double bond content comes from the linoleic and linolenic fatty acid constituents. The $^{13}$C NMR spectrum for soybean oil fatty acids shows multiple vinylic carbon peaks (figure 7-5).
Linseed oil fatty acids contain approximately 9% saturated, 17% oleic, 14% linoleic, and 60% linolenic fatty acids. Integration of the $^1$H NMR spectrum for linseed oil fatty acids yields **2.4 double bonds per fatty acid**. In like manner to soybean oil fatty acids, the higher double bond content comes from the linoleic and linolenic fatty acid constituents. The $^{13}$C NMR spectrum for linseed oil fatty acids shows multiple vinylic carbon peaks and higher contribution from the polyunsaturated fatty acids (figure 7-6).
Figure 7-6. $^{13}$C NMR spectrum for linseed oil fatty acids.

Copolymer Synthesis

5 mol% HEMA copolymers were synthesized by adding 3 g (0.023 mole) of HEMA, 21.9 g (0.219 mole) of MMA, and 28.1 g (0.219 mole) of BA with 100 mL of benzene in a 250 mL three-neck round bottom flask equipped with a magnetic stir bar, water condenser, and a thermocouple. 0.757 g (5 mmole) of recrystallized azobisisobutyronitrile (AIBN) was added to the flask and the contents heated to 75°C. The solution was allowed to react for 24 hours (corresponding to approximately 4 AIBN half-lives). A spatula tip amount of hydroquinone (HQ) was added to terminate the polymerization, and the flask was allowed to cool to ambient temperature.
10 mole% and 20 mole% HEMA copolymers were synthesized via a similar reaction procedure. 10 mole% HEMA copolymers were synthesized using 5 g (0.038 mole) of HEMA, 17.3 g (0.173 mole) of MMA, 22.2 g (0.173 mole) of BA, and 0.631 g of AIBN. 20 mole% HEMA copolymers contained 5 g (0.038 mole) of HEMA, 7.7 g (0.077 mole) of MMA, and 9.849 g (0.077 mole) of HEMA, and 0.315 g (0.002 mole) of AIBN. The copolymers were characterized via $^{13}$C NMR spectroscopy (Figures 7-7 to 7-9).

![Figure 7-7. 5 mole% HEMA copolymer $^{13}$C NMR spectrum.](image)
Figure 7-8. 10 mole% HEMA copolymer $^{13}$C NMR spectrum.
Stearic Acid Functionalization

Benzene solutions containing stoichiometric proportions of stearic acid and DCC were added to the HEMA copolymer solutions. The mixture was stirred overnight and then placed in the freezer to crystallize the DCU. Table 7-1 shows the amounts of stearic acid and DCC incorporated into the 5, 10, and 20 mole% HEMA copolymers.
Table 7-1. Stearic Acid Functionalization Quantities

<table>
<thead>
<tr>
<th>HEMA Copolymer</th>
<th>Reagent</th>
<th>Mass (g)</th>
<th>Moles</th>
</tr>
</thead>
<tbody>
<tr>
<td>5 mole%</td>
<td>Stearic acid</td>
<td>6.6</td>
<td>0.023</td>
</tr>
<tr>
<td></td>
<td>DCC</td>
<td>4.8</td>
<td>0.023</td>
</tr>
<tr>
<td>10 mole%</td>
<td>Stearic acid</td>
<td>10.9</td>
<td>0.038</td>
</tr>
<tr>
<td></td>
<td>DCC</td>
<td>7.9</td>
<td>0.038</td>
</tr>
<tr>
<td>20 mole%</td>
<td>Stearic acid</td>
<td>10.9</td>
<td>0.038</td>
</tr>
<tr>
<td></td>
<td>DCC</td>
<td>7.9</td>
<td>0.038</td>
</tr>
</tbody>
</table>

The stearic acid functionalized copolymers were characterized via $^{13}$C NMR spectroscopy (Figures 7-10 to 7-12). All reactions showed the disappearance of the fatty acid carbonyl peak at 180 PPM. Only the spectra of 20 mol% HEMA oleic, soybean oil, and linseed oil fatty acid functionalized samples had resonances at 174 PPM represented the fatty acid-HEMA ester site. The product ester peak for the 5 and 10 mol% samples was too weak to detect and thus could not be distinguished from the polymer ester peak at 176 PPM. All of the samples contained varying amounts of DCU byproduct as evidenced by the DCU carbonyl peak at 157 PPM. Also, some samples still contained residual benzene as evidenced by the peak at 130 PPM.
Figure 7-10. 5 mole% HEMA stearic acid copolymer $^{13}$C NMR spectrum.

Figure 7-11. 10 mole% HEMA stearic acid copolymer $^{13}$C NMR spectrum.
Figure 7-12. 20 mole% HEMA stearic acid copolymer $^{13}$C NMR spectrum.

Oleic Acid Functionalization

Stoichiometric proportions of oleic acid and DCC were added to 50 mL of benzene, and the blend was added to the HEMA copolymer solutions. Table 7-2 shows the amounts of oleic acid and DCC incorporated into the 5, 10, and 20 mole% HEMA copolymers. The reaction was stirred overnight and then placed in the freezer to crystallize the DCU.
Table 7-2. Oleic Acid Functionalization Quantities

<table>
<thead>
<tr>
<th>HEMA Copolymer</th>
<th>Reagent</th>
<th>Mass (g)</th>
<th>Moles</th>
</tr>
</thead>
<tbody>
<tr>
<td>5 mole%</td>
<td>Oleic acid</td>
<td>10.9</td>
<td>0.038</td>
</tr>
<tr>
<td></td>
<td>DCC</td>
<td>7.9</td>
<td>0.038</td>
</tr>
<tr>
<td>10 mole%</td>
<td>Oleic acid</td>
<td>10.9</td>
<td>0.038</td>
</tr>
<tr>
<td></td>
<td>DCC</td>
<td>7.9</td>
<td>0.038</td>
</tr>
<tr>
<td>20 mole%</td>
<td>Oleic acid</td>
<td>10.9</td>
<td>0.038</td>
</tr>
<tr>
<td></td>
<td>DCC</td>
<td>7.9</td>
<td>0.038</td>
</tr>
</tbody>
</table>

The oleic acid functional copolymers were characterized via $^{13}$C NMR spectroscopy (Figures 7-13 to 7-15).

Figure 7-13. 5 mole% HEMA oleic acid copolymer $^{13}$C NMR spectrum.
Figure 7-14. 10 mole% HEMA oleic acid copolymer $^{13}$C NMR spectrum.

Figure 7-15. 20 mole% HEMA oleic acid copolymer $^{13}$C NMR spectrum.
Soy Fatty Acid Functionalization

Stoichiometric proportions of soybean oil fatty acids and DCC were added to 50 mL of benzene, and then added to the HEMA copolymer solutions. Table 7-3 shows the amounts of soybean oil fatty acids and DCC incorporated into the 5, 10, and 20 mole% HEMA copolymers. The reaction was stirred overnight and then placed in the freezer to crystallize the DCU.

Table 7-3. Soy Fatty Acid Functionalization Quantities

<table>
<thead>
<tr>
<th>HEMA Copolymer</th>
<th>Reagent</th>
<th>Mass (g)</th>
<th>Moles</th>
</tr>
</thead>
<tbody>
<tr>
<td>5 mole%</td>
<td>Soybean oil fatty acids</td>
<td>6</td>
<td>0.023</td>
</tr>
<tr>
<td></td>
<td>DCC</td>
<td>4.8</td>
<td>0.023</td>
</tr>
<tr>
<td>10 mole%</td>
<td>Soybean oil fatty acids</td>
<td>10</td>
<td>0.038</td>
</tr>
<tr>
<td></td>
<td>DCC</td>
<td>7.9</td>
<td>0.038</td>
</tr>
<tr>
<td>20 mole%</td>
<td>Soybean oil fatty acids</td>
<td>10</td>
<td>0.038</td>
</tr>
<tr>
<td></td>
<td>DCC</td>
<td>7.9</td>
<td>0.038</td>
</tr>
</tbody>
</table>

The soybean oil fatty acid functional copolymers were characterized via $^{13}$C NMR spectroscopy (Figures 7-16 to 7-18).
Figure 7-16. 5 mole% HEMA soy fatty acid copolymer $^{13}$C NMR spectrum.

Figure 7-17. 10 mole% HEMA soy fatty acid copolymer $^{13}$C NMR spectrum.
Figure 7-18. 20 mole% HEMA soy fatty acid copolymer $^{13}$C NMR spectrum.

**Linseed Fatty Acid Functionalization**

Stoichiometric proportions of soybean oil fatty acids and DCC were added to 50 mL of benzene, and then added to the HEMA copolymer solutions. Table 7-4 shows the amounts of soybean oil fatty acids and DCC incorporated into the 5, 10, and 20 mole% HEMA copolymers. The reaction was stirred overnight and placed in the freezer to crystallize the DCU.
Table 7-4. Linseed Fatty Acid Functionalization Quantities

<table>
<thead>
<tr>
<th>HEMA Copolymer</th>
<th>Reagent</th>
<th>Mass (g)</th>
<th>Moles</th>
</tr>
</thead>
<tbody>
<tr>
<td>5 mole%</td>
<td>Linseed oil fatty acids</td>
<td>6</td>
<td>0.023</td>
</tr>
<tr>
<td></td>
<td>DCC</td>
<td>4.8</td>
<td>0.023</td>
</tr>
<tr>
<td>10 mol %</td>
<td>Linseed oil fatty acids</td>
<td>10</td>
<td>0.038</td>
</tr>
<tr>
<td></td>
<td>DCC</td>
<td>7.9</td>
<td>0.038</td>
</tr>
<tr>
<td>20 mol %</td>
<td>Linseed oil fatty acids</td>
<td>10</td>
<td>0.038</td>
</tr>
<tr>
<td></td>
<td>DCC</td>
<td>7.9</td>
<td>0.038</td>
</tr>
</tbody>
</table>

The linseed oil fatty acid functional copolymers were characterized via $^{13}$C NMR spectroscopy (Figures 7-19 to 7-21).

Figure 7-19. 5 mole% HEMA linseed fatty acid copolymer $^{13}$C NMR spectrum.
Figure 7-20. 10 mole% HEMA linseed fatty acid copolymer $^{13}$C NMR spectrum.

Figure 7-21. 20 mole% HEMA linseed fatty acid copolymer $^{13}$C NMR spectrum.
GPC Analysis

GPC analysis indicated broad polydispersity indexes (PDI) for the copolymers, ranging from 2.27 to 7.31. Weight average molecular weight ($M_w$) values ranged from 26,265 to 118,665 g/mol, while the number average molecular weight ($M_n$) values ranged from 5,607 to 32,256 g/mol. These numbers were expected as the polymerization process was relatively uncontrolled. A low molecular weight peak (approximately 500 g/mol) was observed in most copolymers and was attributed to unreacted fatty acyl-urea intermediates. Figure 7-22 shows the composite GPC chromatograms for the fatty acid functionalized copolymers. The linseed and soybean oil fatty acid copolymers appear to have the greatest amount of functionalization as supported by the high molecular weight shoulders. Table 7-5 shows the $M_n$, $M_w$, and PDI values for each copolymer.
Figure 7-22. GPC traces for the fatty acid functionalized copolymers.

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### Table 7-5. Molecular Weight and Polydispersity Data for the Fatty Acid Functionalized Copolymers

<table>
<thead>
<tr>
<th>Copolymer</th>
<th>M&lt;sub&gt;w&lt;/sub&gt; (g/mol)</th>
<th>M&lt;sub&gt;n&lt;/sub&gt; (g/mol)</th>
<th>PDI</th>
</tr>
</thead>
<tbody>
<tr>
<td>5% Nonfunctional</td>
<td>40,987</td>
<td>5,607</td>
<td>7.31</td>
</tr>
<tr>
<td>10% Nonfunctional</td>
<td>42,022</td>
<td>6,535</td>
<td>6.43</td>
</tr>
<tr>
<td>20% Nonfunctional</td>
<td>26,265</td>
<td>11,558</td>
<td>2.27</td>
</tr>
<tr>
<td>5% Stearic</td>
<td>60,277</td>
<td>18,433</td>
<td>3.27</td>
</tr>
<tr>
<td>10% Stearic</td>
<td>52,481</td>
<td>13,784</td>
<td>3.81</td>
</tr>
<tr>
<td>20% Stearic</td>
<td>32,860</td>
<td>9,722</td>
<td>3.38</td>
</tr>
<tr>
<td>5% Oleic</td>
<td>60,063</td>
<td>16,657</td>
<td>3.61</td>
</tr>
<tr>
<td>10% Oleic</td>
<td>94,557</td>
<td>23,455</td>
<td>4.03</td>
</tr>
<tr>
<td>20% Oleic</td>
<td>35,508</td>
<td>12,704</td>
<td>2.80</td>
</tr>
<tr>
<td>5% Soybean</td>
<td>54,829</td>
<td>17,110</td>
<td>3.2</td>
</tr>
<tr>
<td>10% Soybean</td>
<td>58,368</td>
<td>18,634</td>
<td>3.13</td>
</tr>
<tr>
<td>20% Soybean</td>
<td>46,321</td>
<td>15,674</td>
<td>2.96</td>
</tr>
<tr>
<td>5% Linseed</td>
<td>118,665</td>
<td>17,211</td>
<td>6.89</td>
</tr>
<tr>
<td>10% Linseed</td>
<td>83,597</td>
<td>32,256</td>
<td>2.59</td>
</tr>
<tr>
<td>20% Linseed</td>
<td>65,770</td>
<td>15,607</td>
<td>4.21</td>
</tr>
</tbody>
</table>

The fatty acid functionalized copolymers were applied on salt plates for FTIR analysis. One set of samples was dried at ambient conditions, while another was force cured at 100°C for 7 days. The films were characterized via FTIR studies.
FTIR Studies

Figures 7-23 to 7-28 show the partial FTIR spectra (2800-3100 cm\(^{-1}\)) for ambient and force cured films of the 20% HEMA copolymer functionalized with oleic acid, soybean oil fatty acids, and linseed oil fatty acids. The base copolymer and the stearic acid functionalized copolymer spectra are not shown here as they lack the cis-unsaturation. All spectra were normalized to the ester peak at 1730 cm\(^{-1}\). The cis-unsaturation peak (3010 cm\(^{-1}\)) of the functionalized 5 and 10 mole% HEMA copolymers were too low to be distinguished via FTIR.

Figure 7-23 shows the FTIR spectra for ambient cured oleic acid functionalized copolymers. The cis-unsaturation remained unchanged during the drying process due to the high activation energy of the primary auto-oxidation process. The monoallylic hydrogen atoms of oleic acid are less abstractable than bisallylic hydrogen atoms found in linoleic (2 unconjugated double bonds) and linolenic (3 unconjugated double bonds) fatty acids. Moreover, the active methylene group situated between the double bonds lowers the activation energy for hydroperoxide formation in linolenic and linoleic fatty acids, often rearranging to form conjugated materials.\(^7\) However, force curing the copolymer at 100°C provides sufficient energy for auto-oxidation of the oleic unsaturation, and the cis-unsaturation is completely consumed by day 3 of curing (Figure 7-24). The loss in peak intensity for the C-H stretch at 2800 – 3000 cm\(^{-1}\) for the force cure samples is due to the evaporation of residual benzene and does not affect measurements of the unsaturation as all spectra are normalized to the ester.

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Figure 7-23. FTIR spectra for oleic acid functionalized copolymer (20% HEMA) cured at ambient.

Figure 7-24. FTIR spectra for oleic acid functionalized copolymer (20% HEMA) cured at 100°C.
Figure 7-25 shows the FTIR spectra for ambient cured, soybean oil fatty acid functionalized copolymers. Soybean oil contains 15% saturated, 22% oleic, 55% linoleic, and 8% linolenic fatty acids. This confirms that the higher concentration of bisallylic hydrogen atoms promotes auto-oxidation under ambient curing conditions by day 7.

![FTIR spectra for soybean oil fatty acids functionalized copolymer (20% HEMA) cured at ambient.](image)

Figure 7-25. FTIR spectra for soybean oil fatty acids functionalized copolymer (20% HEMA) cured at ambient.

Figure 7-26 shows the FTIR spectra for soybean oil fatty acid functionalized copolymers force cured at 100°C. As observed for the force cured oleic acid functionalized copolymers, complete loss of cis-unsaturation is observed by day 3.
Figure 7-26. FTIR spectra for soybean oil fatty acids functionalized copolymer (20% HEMA) cured at 100°C.

Figure 7-27 shows the FTIR spectra for ambient cured linseed oil fatty acid functionalized copolymers. Linseed oil contains 9% saturated, 17% oleic, 14% linoleic, and 60% linolenic fatty acids. The high concentration of linolenic fatty acid results in complete auto-oxidation in under 3 days of ambient curing.

Figure 7-28 shows the FTIR spectra for linseed oil fatty acid functionalized copolymers force cured at 100°C. Complete loss of cis-unsaturation is noted by day 3.
Figure 7-27. FTIR spectra for linseed oil fatty acids functionalized copolymer (20% HEMA) cured at ambient.

Figure 7-28. FTIR spectra for linseed oil fatty acids functionalized copolymer (20% HEMA) cured at 100°C.
Gel Content

All the copolymers were cured at 100°C for 1 week before gel content analysis. The base copolymer and the stearic acid copolymers were completely soluble in methylene chloride whereas copolymers containing oleic acid, soybean oil fatty acids, and linseed oil fatty acids contained varying amounts of gel fractions (Table 7-6).

Table 7-6. Gel Content Data

<table>
<thead>
<tr>
<th>Copolymer</th>
<th>Gel Content (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5% Oleic acid copolymer</td>
<td>5</td>
</tr>
<tr>
<td>10% Oleic acid copolymer</td>
<td>18</td>
</tr>
<tr>
<td>20% Oleic acid copolymer</td>
<td>4</td>
</tr>
<tr>
<td>5% Soybean fatty acids copolymer</td>
<td>22</td>
</tr>
<tr>
<td>10% Soybean fatty acids copolymer</td>
<td>21</td>
</tr>
<tr>
<td>20% Soybean fatty acids copolymer</td>
<td>38</td>
</tr>
<tr>
<td>5% Linseed fatty acids copolymer</td>
<td>40</td>
</tr>
<tr>
<td>10% Linseed fatty acids copolymer</td>
<td>70</td>
</tr>
<tr>
<td>20% Linseed fatty acids copolymer</td>
<td>66</td>
</tr>
</tbody>
</table>

The gel content data did not exhibit a linear trend for the oleic acid functionalized copolymer, i.e., it does not increase with increasing fatty acid functionalization. High gel content (~18%) was noted for the 10% oleic acid functionalized copolymer over the 5 and 20% samples. This inconsistency may be due to incomplete oleic acid functionalization of the 20% copolymer. The 10 and 20% linseed oil fatty acid functionalized copolymers exhibited the highest gel fractions at 70 and 66%, respectively.

Summary

VOMMs are useful coalescing aids and film performance enhancers, but chain transfer reactions consume the fatty acid unsaturation and limit the auto-oxidation capability of VOMM polymers. VOMM-based polymers synthesized in
the absence of chain transfer reactions were required to ensure complete retention of allylic hydrogen atoms. DCC coupling proved to be a useful method of coupling fatty acids with (meth)acrylate copolymers without involving chain transfer processes. FTIR analysis showed complete auto-oxidation of the 20 mol % copolymers containing oleic, soybean oil fatty acids, and linseed oil fatty acids after 3 days of force cure at 100°C. All of the force cured fatty acid functionalized copolymers contained significant gel fractions. Future experiments will focus on functionalizing copolymers with higher molecular weights and glass transition temperatures and adapting the synthesis to emulsion copolymerization conditions.
References:

CHAPTER VIII

CONCLUSIONS

Vegetable oils continue to prove useful as feedstock materials for a large variety of industrial products, including polymers for coatings, due to their variety, sustainability, and cost effectiveness. When used in coatings, VOMMs yield polymers with increased flexibility and potential for $T_g$ enhancement, while simultaneously reducing dependence on petroleum and eliminating VOC emissions. Bio-based polymers are finding use in application areas that were once strictly dominated by petrochemicals. In our research, the role of cis-unsaturation had not been fully explored in some of these new application areas. To that end, VOMMs in three different systems were explored to determine the involvement of cis-unsaturation in chain transfer, auto-oxidation, and copolymerization reactions. VOMMs were employed in UV curable thiol-ene coatings, UV cationic coatings, and acrylic solution copolymers, and several fundamental studies were conducted to determine how and to what extent cis-unsaturation contributes to thin film performance properties.

Novel castor VOMMs were successfully synthesized to include acrylate, vinyl ether, and allyl ether functionalities. These bio-based prepolymers were blended with trifunctional thiols and an alpha-cleavage photoinitiator to yield VOC-free UV curable formulations. The final films contained approximately 40% vegetable oil by weight and exhibited maximum flexibility at 28% elongation, high solvent resistance, good hardness, and excellent adhesion to steel. Moreover, it was observed after one week of aging that many of the physical properties such
as solvent and impact resistance increased without a measurable loss in flexibility. This increase in physical properties was due to an increase in crosslink density brought about by continued reaction between vinyl moieties, thiols, and cis-unsaturation. FTIR analysis indicated that the postcure reaction was primarily continued thiol-ene reaction, also known as "dark cure".

Cis-unsaturation was involved in the initial curing reaction and, to a lesser degree, in postcure crosslinking. Its behavior was determined to be ene dependent. Vinyl ethers normally react stoichiometrically with thiols in simple vinyl ether-thiol photopolymerizations, but it was observed in the vinyl ether functional castor VOMM systems, that vinyl ethers reached higher levels of conversion as compared to the thiol comonomer. This was due to competitive copolymerization of vinyl ethers and cis-unsaturation in addition to vinyl ether-thiol polymerization. In the allyl ether functional castor VOMM systems the thiols reacted to higher conversions than the allyl ether group. In these systems, thiols react with cis-unsaturation in addition to the terminal allyl ether functionality during UV curing. It is commonly observed when polymerizing acrylates with thiols that the acrylate group will undergo significant homopolymerization in addition to reacting in the thiol-ene step-growth mechanism. This phenomena was also observed in our acrylate systems. Cis-unsaturation also contributes to film build in these systems. Cis-unsaturation behaved very differently in each of these systems but was always involved in initial curing, and made some contribution to post-curing reactions.
Thiol-ene photopolymerizations resulted in homogeneous networks due to the highly regular step-growth addition reactions and high conversions that can be attained with many of these systems. DMA analysis of films produced by photopolymerization of low molecular weight enes and thiols showed very small widths at half-height (tan δ response), indicating a high level of homogeneity in the crosslinked networks. The thiol-vinyl ether system displayed the narrowest tan δ response with a width at half-height of approximately 10°C, consistent with strict adherence to the thiol-ene polymerization mechanism. The thiol-vinyl ether-acrylate system had a larger width at half-height (approximately 20°C) and the thiol-acrylate system had an even larger width at half-height (approximately 30°C). The broader tan δ response was due to acrylate homopolymerization occurring in addition to thiol-ene polymerization. The width at half-height for the castor-VOMM thiol-ene formulations ranged from 30°C to 50°C, indicating a crosslinked network with even greater heterogeneity. This is due in part to non-uniformity in the castor VOMM chemical structures and due to the mixture of concurrent reactions that occur during thiol-ene photopolymerization and "dark cure".

The majority of cationic photopolymerizations involve epoxy end-functional aliphatic and cycloaliphatic prepolymers but epoxidized soybean oil has found use in some applications. Fully epoxidized soybean oil is generally employed for these applications as it has the maximum number of reaction sites. The cationic photopolymerization of partially epoxidized soybean oil yields films that are too lightly crosslinked to serve any commercial purpose. However, the influence of
free radical decomposition byproducts have not been investigated in these
photopolymerization reactions. Since free radicals are formed as byproducts in
the decomposition of cationic photoinitiators, it was our intention to determine if
they could foster free radical polymerization of the cis-unsaturation in partially
epoxidized soybean oil. In other words, can they mimic or accelerate auto­
oxidation when partially epoxidized soybean oil is photopolymerized?

It was determined using FTIR spectroscopy that free radicals generated
by cationic photoinitiator decomposition did not influence auto-oxidation when
produced in the presence of partially epoxidized soybean oil. Partially epoxidized
soybean oil was successfully synthesized to yield products that contained varying
levels of residual cis-unsaturation. However, this unsaturation did not participate
to any appreciable amount in film building reactions when photopolymerized.
The low reactivity of this double bond may be one reason for its failure to react.
Also, radical combination with molecular oxygen dissolved in the coating or with
anti-oxidants may have deactivated the alkyl and aryl radicals before reaction
with cis-unsaturation and/or allylic hydrogen atoms. Formation of alkyl- and
arylperoxides is energetically favored over hydrogen abstraction. The cis­
unsaturation was consumed over the course of two weeks of “dark cure” in the
ambient and UV-cured samples, but remained unaffected in samples placed in a
nitrogen-purged dry box. The consumption of cis-unsaturation can be attributed
to natural auto-oxidative polymerization.

Perhaps the largest application area for VOMMs is in waterborne coatings.
Our research group has been investigating the use of VOMMs in emulsions for
more than a decade. Here the focus is on lowering minimum filming temperatures VOMMs' copolymerization with traditional monomers such as methylmethacrylate and butyl acrylate, thereby reducing or eliminating the need to formulate with VOCs. Additionally, allowing post application crosslinking of the same lower $T_g$ copolymers to increase $T_g$ after application via auto-oxidation is very beneficial in terms of increasing the environmental compliance of a coating with little-to-no increase in cost. Unfortunately, when VOMMs are polymerized as comonomers in emulsion polymerization chain transfer reactions between polymer radicals and VOMMs reduce auto-oxidation potential and the polymer's molecular weight. In situ FTIR studies of solution polymerizations performed in the presence of fatty acid moieties indicate that unsaturated fatty acids, fatty acid derivatives, and triglycerides reduced polymerization rates but not beyond practical utility with many models and the particular VOMMs as studied in our group. The retardation in polymerization rate increased with the amount of unsaturation and conjugated unsaturation. Vegetable oils containing significant amounts of fatty acids having bisallylic hydrogen atoms, such as linoleic and linolenic fatty acids, were found to be more reactive towards chain transfer than those with monoallylic hydrogen atoms, such as oleic acid. One model, a conjugated double bond system of $\alpha$-eleostearic acid (tung oil), inhibited nearly all polymerization. In contrast, the polymerization rate was unaffected by stearic acid, PEG, and PEG modified stearate. While PEG did not affect the polymerization rate, chain transfer can occur if hydroperoxides are present prior to polymerization.
\(^1\text{H} \) NMR spectroscopy studies were used to confirm whether chain transfer occurs by abstraction of allylic hydrogen atoms or by addition to the vinylic double bond of the fatty acids in these systems. These studies indicated that MMA homopolymerization in the presence of soybean oil had little effect on the unsaturation content, yet molecular weight was reduced in comparison with control polymers. This means that abstraction of allylic hydrogen atoms by the growing polymer chains is the more energetically favored reaction. GPC analysis indicated that the resulting allylic radicals do not couple with growing polymer chains at low monomer conversions (< 5\%). Coupling can occur at longer reaction times when there is less unreacted monomer is present and more opportunity for the relatively large vegetable oil structures to encounter polymer radicals.

In view of the fact that VOMMs are involved in chain transfer reactions, it is important to know what kind of property development can be expected when all of the allylic hydrogen atoms and unsaturation are preserved throughout the polymerization process and are available to post-application crosslinking. In order to produce such benchmark data, DCC coupling was employed as it is a mild synthetic technique which can be performed in the absence of radicals. Several VOMM functionalized meth(acrylic) polymers were produced through the DCC assisted esterification of HEMA copolymers with fatty acids. Stearic acid functionalized copolymers were used as the control. Unsaturation was altered in these systems by introducing various unsaturated fatty acids into the copolymer backbone, namely, oleic acid, soybean oil fatty acids, and linseed oil fatty acids.
FTIR analysis indicated that consumption of unsaturation increased in order of oleic acid, soybean oil fatty acid, and linseed oil fatty acid functionalized copolymers when cured under ambient conditions. However, complete auto-oxidation for all of the unsaturated copolymers was noted after 3 days of force cure at 100°C, a different mechanisms and yet proof of allylic unsaturations presence and potential for usable retention of auto-oxidizable moieties after free radical polymerization. Force cured linseed oil fatty acid copolymers contained significant gel fractions (greater than 65%) while oleic acid and soybean oil fatty acid functionalized copolymers contained gel fractions to a lesser degree. The increased reactivity of the linseed fatty acid copolymers is due to the higher concentrations of linoleic and linolenic fatty acids as composite fatty acids. The bisallylic hydrogen atoms are more easily abstractable than monoallylic hydrogen atoms allowing for facile primary auto-oxidation.

The research discussed in this dissertation has expanded our understanding of how cis-unsaturation behaves in thiol-ene photopolymerization, cationic photopolymerization, and free-radical solution copolymerization. It was determined that cure mechanism, polymerization conditions, and comonomer composition dictate the extent to which cis-unsaturation enhances or reduces coating properties. The castor VOMMs used in the thiol-ene coatings produced high gloss films with excellent physical properties which increased as the films aged. It was found that fully epoxidized soybean oil produced tractable films when cationically photopolymerized and that free-radical polymerization does not function as a viable secondary cure mechanism when polymerizing partially
epoxidized soybean oil. Chain transfer reactions do occur when polymerizing VOMMs as comonomers, and this can negatively impact polymer molecular weight and post-application crosslinking. VOMMs can be incorporated into acrylic polymers through non-radical reaction pathways, however, and similar reactions may be adapted to emulsion polymerization in order to prevent molecular weigh reduction and loss of allylic hydrogen atoms and cis-unsaturation. This research contributes to the design of VOMM-based coatings and further expands VOMM-based technology.
CHAPTER IX

FUTURE WORK SECTION

Substantial progress has been achieved in furthering our understanding of the benefits as well as the limitations of VOMM-based technology. There is still much room for growth and ideas for future research are proposed in this chapter. They are 1) quantifying how much chain transfer occurs when free radical polymerizations using VOMMs as comonomers are performed at reduced temperatures, 2) using DCC coupling to functionalize high molecular weight latexes, 3) exploring a cost effective method of attaching vegetable oil derivatives to emulsion polymers using a non-radical, \textit{in situ} method, and 4) producing lower viscosity thiol-ene coatings.

\textbf{Chain Transfer Experiments at Reduced Temperatures}

Chain transfer is proven to occur at 75°C when polymerizing acrylic monomers in the presence of vegetable oil derivatives as detailed in chapter 6. However, copolymerizing VOMMs is the simplest and most economically viable method of incorporation into emulsion polymers. Optimization of the polymerization conditions may be all that is required to keep chain transfer events low and in favor of monomer propagation. Hydrogen abstraction reactions have a higher activation energy than vinylic addition reactions, and therefore have higher temperature dependence than addition reactions.\textsuperscript{1}

Lowering the reaction temperature below the activation energy for allylic hydrogen abstraction should allow for slower monomer propagation in the absence of chain transfer.
The same polymerization conditions as stated in the \textit{in situ} FTIR section of chapter 6 should be followed with the exception of initiator choice and temperature. A more reactive initiator is required in place of AIBN to maintain a high radical flux. Redox initiation of acyl peroxides with amines has been documented in organic media.\textsuperscript{2,3} As a starting point, benzoyl peroxide with $N,N$-dialkyl aniline is a good choice for the initiator system. Odian reported the dissociation constant ($k_d$) for styrene polymerization at 90°C using benzoyl peroxide to be $1.33 \times 10^{-4}$ sec$^{-1}$ ($t_{1/2} = 1.44$ hours). When using a benzoyl peroxide-$N,N$-diethylaniline redox system, the $k_d$ was $1.25 \times 10^{-2}$ sec$^{-1}$ ($t_{1/2} = 0.015$ hours) at 60°C and $2.29 \times 10^{-3}$ (0.084 hours) at 30°C.\textsuperscript{4} With the appropriate redox initiator package, 9-33 wt% vegetable oil derivative should be added to MMA and BA polymerizations conducted at 30°C and 50°C as a starting point.

**DCC Coupling with Emulsion Polymers**

The molecular weights obtained during solution copolymerization of MMA, BA, and HEMA were approximately 50,000 g/mol (Chapter 7). Emulsion polymers typically range in molecular weight from 100,000 to 1,000,000 g/mol. Functionalizing emulsion polymers is expected to yield results that are more representative of commercial systems. A copolymer of HEMA and MMA (1:5 on a molar basis) will have a theoretical $T_g$ of 91°C.\textsuperscript{5} Functionalizing this copolymer with a fatty acid via DCC coupling will yield a polymer with a sufficient $T_g$ for DMA analysis. A starting formulation for the emulsion is recommended to include sodium laurel sulfate (2 phr or less), CO-887 (ethoxylated nonylphenol) (2 phr or
less), ammonium persulfate (0.5 phr), and sodium bicarbonate (0.1 phr). It is also recommended that the polymerization be performed using batch emulsion conditions at 85°C and 1800 rpm.

Upon completion of the polymerization, the emulsion should be separated with methylene chloride, and the organic layer will be dried over magnesium sulfate. The polymer solution should then be vacuum filtered to remove magnesium sulfate. The polymer can now be functionalized with fatty acids. Stearic acid, oleic acid, soybean oil fatty acids, and linseed oil fatty acids should first be reacted with DCC and then added to the polymer/methylene chloride solution. Separately, HEMA should be functionalized with fatty acids prior to emulsion polymerization and then copolymerized with MMA via emulsion polymerization.

Ambient and force cure auto-oxidation studies should be performed in like manner to those mentioned in Chapter 7. Analysis via FTIR, DSC, and DMA would quantify the ability of these fatty acid functionalized polymers to cure via auto-oxidation. For molecular weight determination, the polymers should be converted to their respective poly(methacrylic acid) sodium salts via base catalyzed hydrolysis, and examined using aqueous GPC with poly(methacrylic acid) sodium salt standards. The experiments allow for the exact determination of the polymer’s molecular weight. Comparing the molecular weight obtained for both polymers would indicate the extent that chain transfer reduces molecular weight.
Novel Non-Radical Processes to Attach VOMMs

While DCC coupling is an excellent means of attaching VOMMs in organic media, it is ineffective in reacting carboxylic acids and alcohols in aqueous environments as it proceeds via dehydration. In the presence of water, the equilibrium shifts towards carboxylic acid and alcohol formation rather than ester formation. Therefore, novel methods are required to attach VOMMs to acrylic polymers in emulsions.

A somewhat exotic, yet economical way of accomplishing this makes use of in situ generation of isocyanates from amides using alkali hypohalides such as sodium hypochlorite (NaOCl). Any nucleophile can then be introduced for reaction with the pendent isocyanate groups. Figure 9-1 shows the proposed in situ isocyanate generation in an acrylamide polymer with post-added 1) fatty acid and 2) soyamide. Soyamide can be used as the favored nucleophile since the alcohol-isocyanate reaction proceeds more rapidly than the carboxylic acid–isocyanate reaction.
Figure 9-1. Fatty acid copolymer synthesis using in situ isocyanate generation.

The isocyanate group can also readily react with water to form carbamic acid followed by carbon dioxide elimination to yield an amine. The stable amine can then be reacted with fatty acids (Figure 9-2). This reaction may pose problems, however, due to difficulty in condensing water during reaction and competing trans-amidation reactions.
While the thiol-ene UV curable coatings formulated with VOMMs based on IPDI and castor oil produced excellent coatings, they displayed high viscosities (Table 9-1). For reference, the viscosity of water and honey is 0.01 poise and 30 poise, respectively. Perhaps the simplest way of reducing the viscosity is to simply heat the coating immediately before application. This would disassociate the hydrogen bonding imparted from the urethane functionality and allow the applicator to adjust the temperature to reach the desired application viscosity. Another method of reducing the viscosity is to add a reactive diluent such as hexanediol diacrylate or trimethylolpropane triacrylate. Acrylates are sensitizers, however, and it would be better if they were excluded from the formulation.
Table 9-1. Viscosity of Thiol-Ene Coatings

<table>
<thead>
<tr>
<th>Material</th>
<th>Viscosity (Poise)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formulation 1</td>
<td>216</td>
</tr>
<tr>
<td>Formulation 2</td>
<td>219</td>
</tr>
<tr>
<td>Formulation 3</td>
<td>345</td>
</tr>
<tr>
<td>Formulation 4</td>
<td>345</td>
</tr>
<tr>
<td>Formulation 5</td>
<td>336</td>
</tr>
<tr>
<td>Formulation 6</td>
<td>333</td>
</tr>
</tbody>
</table>

A better method of reducing the viscosity is to alter the VOMM synthesis. Polyethylene glycol (PEG) could be reacted with the vinyl monomer-IPDI adduct, and the excess PEG hydroxyls could be reacted with IPDI to form a vinyl monomer-IPDI-PEG-IPDI adduct. The vinyl monomer-IPDI-PEG-IPDI adduct can then be reacted with castor oil to provide a PEG modified castor-VOMM. The length of the PEG unit can be varied to achieve the desired viscosity. Figure 9-3 shows the synthetic method for PEG modified vinyl ether functional castor-VOMM. However, the reduction in viscosity will be achieved at the expense of lowering vegetable oil content and increasing water sensitivity within the coating.
Figure 9-3. Synthesis of PEG modified vinyl ether functional castor-VOMM.
References:

7) Dougherty, S.M. U.S. 6,013,725.