

# Synthesis of Thermoset Plastics by Lewis Acid Initiated Copolymerization of Fish Oil Ethyl Esters and Alkenes

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Received 10 July 2000; accepted 7 October 2000

**ABSTRACT:** The Lewis acid initiated cationic homopolymerization of Norway fish oil ethyl ester (NFO) or the corresponding conjugated fish oil (CFO) and their copolymerization with various alkene comonomers is investigated. Among the Lewis acids employed, boron trifluoride diethyl etherate (BFE,  $\text{BF}_3 \cdot \text{OEt}_2$ ) is found to be the most effective initiator for cationic polymerization of the NFO and CFO systems. The BFE-initiated homopolymerization of NFO generally results in low molecular weight viscous oils, while that of CFO leads to a solid elastic gel with a gel time of more than 72 h at room temperature. Copolymerization of the NFO or CFO with some alkene comonomers significantly facilitates gelation. The gel times are largely dependent upon the stoichiometry, the type of fish oil, and the alkene comonomer. After postcuring at elevated temperatures, the cationic copolymerization affords polymers ranging from soft rubbery materials to rigid plastics. These NFO and CFO polymers are composed of highly crosslinked materials and a certain amount of free oils and are found to be fully cured thermosets. Generally, CFO polymers appear to be harder than the corresponding NFO polymers. However, the thermal properties of the bulk polymers are similar to each other, and their insoluble extracts exhibit much higher thermal stability than the bulk thermosets. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 81: 2001–2012, 2001

**Key words:** boron trifluoride diethyl etherate; fish oil; cationic polymerization; thermosets

## INTRODUCTION

Biodegradable plastics from renewable natural resources, such as carbohydrates, starch, and protein, have become increasingly interesting because of their low cost, ready availability, and biodegradability. In contrast, relatively little work has been reported on the conversion of fats and oils to high molecular weight polymers. Fish oil is a biodegradable, renewable natural resource. It has been used industrially to produce protective coatings, lubricants, sealants, inks, an-

imal feeds, and surfactants.<sup>1</sup> Natural fish oil has a triglyceride structure with a high percentage of polyunsaturated  $\omega$ -3 fatty acid chains that contain five to six nonconjugated carbon–carbon double bonds.<sup>2</sup> Thus, the high degree of unsaturation makes it possible to polymerize or copolymerize the unsaturated oils into useful polymers.

Fish oil was polymerized thermally to produce varnishes,<sup>3</sup> detergents,<sup>4</sup> and materials used in the canning industry.<sup>5</sup> The mechanism for the thermal polymerization of fish oil is not well defined, but it may proceed by a Diels–Alder process.<sup>6</sup> Fish oil was modified using maleic anhydride to produce industrially useful drying oils,<sup>7</sup> heat resistant varnishes,<sup>8</sup> and plasticizers for poly(vinyl chloride).<sup>9</sup> It was also modified through

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Contract grant sponsor: Iowa Soybean Promotion Board.

*Journal of Applied Polymer Science*, Vol. 81, 2001–2012 (2001)  
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reactions with 1,3-dienes to produce Diels–Alder adducts that were used as drying oils<sup>10</sup>; fast-drying binders for paints<sup>11</sup>; primers for steel and wooden surfaces<sup>12</sup>; coatings for motor vehicles<sup>13</sup>; flexible, waterproof coatings<sup>14</sup>; and for the slow-release of pesticides applied to plants.<sup>15</sup> Fish oil was also extensively utilized in making alkyd resins in the coatings industry.<sup>16</sup> There are also several reports in the literature of the free-radical polymerization and copolymerization of fish oil.<sup>17</sup>

Lewis acids are used to polymerize fish oil derivatives and other natural oils. Epoxidized Menhaden fish oil polymerizes in the presence of catalytic amounts of boron trifluoride diethyl etherate (BFE,  $\text{BF}_3 \cdot \text{OEt}_2$ ) to produce a useful drying oil or insoluble crosslinked polymers, depending on the extent of epoxidation.<sup>18</sup> The free fatty acids<sup>19</sup> and methyl esters of the free fatty acids<sup>20</sup> of soybean oil are polymerized to viscous oils using BFE. Oiticica<sup>21</sup> and linseed<sup>22</sup> oils also polymerize in the presence of boron trifluoride and produce viscous drying oils. The copolymerization of divinylbenzene (DVB) or styrene with linseed oil using catalytic amounts of boron trifluoride reportedly produced oils with useful drying properties.<sup>23</sup>

Although there are many reports in the literature of the production of viscous oils from the polymerization of fish oil, there are very few examples of the direct production of solid polymeric materials. The goal of this research was to synthesize solid thermoset polymers directly from native and conjugated fish oil ethyl esters via BFE-initiated cationic copolymerization with various alkene comonomers.

## EXPERIMENTAL

### Materials

The Norway fish oil (NFO) used in this study was Norwegian Pronova EPAX 5500 EE fish oil ethyl ester (Bergen, Norway). The conjugated fish oil (CFO) was prepared from the NFO in our laboratory by using Wilkinson's catalyst  $[\text{RhCl}(\text{PPh}_3)_3]$ .<sup>24</sup> The degree of conjugation was calculated to be about 90%. The DVB, norbornadiene (NBD), dicyclopentadiene (DCP), styrene, myrcene, phenol, linalool, furfural, *p*-benzoquinone, 2-allylphenol, *p*-mentha-1,8-diene, furan, 1,2-dimethoxybenzene, bisphenol A, 1,3-cyclohexadiene, maleic anhydride, methyl acrylate, vinyl acetate, vinylidene chloride, acrylonitrile, methyl crotonate, acrolein, isoprene,

dimethyl acetylenedicarboxylate, diallyl phthalate, BFE, iron(III) chloride, and tin tetrachloride were obtained from Aldrich Chemical Co. (Milwaukee, WI). Aluminum chloride, zinc chloride, titanium tetrachloride, and concentrated sulfuric acid were purchased from Fisher Scientific (Fair Lawn, NJ). Tin tetrachloride pentahydrate was obtained from Mallinckrodt Chemical Co. (St. Louis, MO). All reagents obtained from commercial vendors were used as received unless otherwise noted.

### Copolymerization

All of the NFO and CFO polymerization reactions were performed on a 2.0-g scale. The amount of each reactant used is reported as a weight percentage. For example, to 1.3 g (65%) of NFO in a 2-dram vial ( $17 \times 60$  mm) was added 0.4 g (20%) of DVB and 0.2 g (10%) of NBD. The reaction mixture was then stirred to ensure homogeneity prior to the addition of 0.1 g (5%) of BFE ( $\text{BF}_3 \cdot \text{OEt}_2$ ). The resulting solution was vigorously stirred and sealed under a nitrogen atmosphere. The reaction was allowed to proceed at 25°C for 24 h, then 60°C for 24 h, and finally 110°C for 72 h to produce 1.94 g (97% yield) of a hard polymer identified by its composition as NFO65-DVB20-NBD10-BFE5.

### Characterization Techniques

#### *Soxhlet Extractions of Bulk NFO and CFO Polymers*

Soxhlet extraction was used to characterize the structure of the bulk polymers. Typically, a 2-g bulk polymer sample was extracted with 100 mL of refluxing solvent ( $\text{CH}_2\text{Cl}_2$  or THF) using a Soxhlet extractor in air for 24 h. After extraction the resulting solution was concentrated and the soluble extract was isolated for further characterization. The remaining insoluble polymeric material was dried under a vacuum prior to further analysis.

#### *Spectroscopy*

<sup>1</sup>H- and <sup>13</sup>C-NMR spectroscopy were used to characterize the starting materials and the soluble materials extracted from the bulk polymers. All of the <sup>1</sup>H- and <sup>13</sup>C-NMR spectra were recorded in  $\text{CDCl}_3$  using a Varian Unity spectrometer at 300 MHz and 75.5 MHz, respectively. Cross-polarization magic angle spinning (CP MAS) <sup>13</sup>C-NMR was performed on the remaining insoluble mate-

rials extracted from the bulk polymers using a Bruker MSL 300 spectrometer. Samples were examined at two spinning frequencies (2500 and 3000) to differentiate between actual signals and spinning side bands.

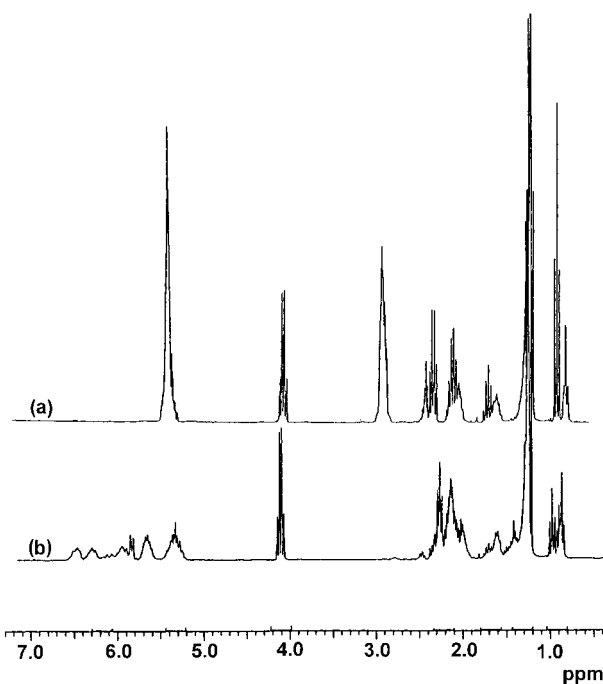
### Thermal Analysis

Differential scanning calorimetry (DSC) was used to measure the phase transitions and postcuring behavior of the bulk polymers. The DSC data were obtained using a Perkin–Elmer Pyris-7 DS calorimeter with a temperature ramp of 20°C/min. Thermogravimetric analysis (TGA) was employed to measure the thermal properties of the bulk polymers, as well as the remaining insoluble materials after extraction by CH<sub>2</sub>Cl<sub>2</sub> or THF. The TGA data were collected using a Perkin–Elmer Pyris-7 TG analyzer. A temperature range of 50–900°C was used with ramps of 20°C/min and purging with a nitrogen or air atmosphere.

## RESULTS AND DISCUSSION

### Molecular Structures of NFO and CFO

Spectrum a in Figure 1 shows the <sup>1</sup>H-NMR spectrum of the regular fish oil ethyl ester (NFO)



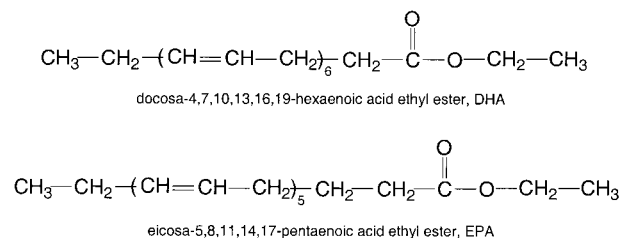
**Figure 1** <sup>1</sup>H-NMR spectra of NFO (spectrum a) and CFO (spectrum b).

**Table I** Fish Oil Fatty Acid (Ethyl Ester) Composition

No. C=C Bonds	%
0	8.90
1	18.20
2	1.10
3	0.99
4	6.03
5 (EPA + DPA)	37.25
6 (DHA)	24.72
Unknown	2.81

employed in this study. The NFO is a mixture of fatty acid ethyl esters ( $\delta = 4.0\text{--}4.3$  ppm) with a high degree of unsaturation (vinylic hydrogens at  $\delta = 5.1\text{--}5.5$  ppm). Table I indicates that the NFO is composed of approximately 90% unsaturated fatty acid ethyl esters.<sup>25</sup> More than 60% of them have five or more nonconjugated C=C bonds. Based on its <sup>1</sup>H-NMR spectrum, the NFO was found to possess 3.6 C=C bonds per molecule on average. The <sup>1</sup>H-NMR spectrum of the conjugated NFO (CFO) in spectrum b in Figure 1 indicates that conjugation does not affect the degree of unsaturation (vinylic hydrogens at  $\delta = 5.1\text{--}6.6$  ppm). Approximately 90% of the C=C bonds are conjugated in the fatty acid ethyl esters.<sup>24</sup>

Figure 2 shows the molecular structures of two of the most important  $\omega$ -3 fatty acid ethyl esters in the NFO: docosa-4,7,10,13,16,19-hexaenoic acid ethyl ester (DHA, 24.72%) and eicosa-5,8,11,14,17-pentaenoic acid ethyl ester (EPA, 31.68%). Conjugating the C=C bonds of the DHA and EPA produced a number of fatty acid ethyl ester isomers, but the number of C=C bonds remained unchanged. The NFO and particularly the CFO were expected to be cationically polymerizable monomers due to the large number of C=C bonds.<sup>26</sup>



**Figure 2** The molecular structures of the representative fatty acid ethyl esters DHA and EPA in the native NFO.

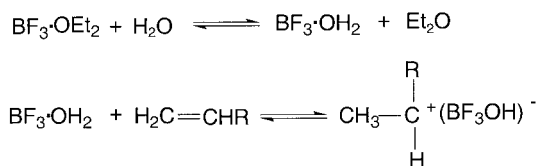
### Initiators for Cationic Homopolymerization and Copolymerization of Fish Oils

Lewis acids (i.e.,  $\text{AlCl}_3$ ,  $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ ,  $\text{TiCl}_4$ ,  $\text{ZnCl}_2$ ,  $\text{FeCl}_3$ ,  $\text{SnCl}_4$ ,  $\text{BCl}_3$ ,  $\text{BF}_3 \cdot \text{OEt}_2$ , and sulfuric acid) were proved to be very effective initiators for cationic polymerization.<sup>26,27</sup> Although the simple homopolymerization of NFO or CFO by the above initiators led to viscous oils in most cases, copolymerization of the NFO or CFO with some alkene comonomers, such as DVB, NBD, and DCP, afforded viable solid polymeric materials. When 30% alkene comonomers are employed, the initiators  $\text{AlCl}_3$ ,  $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ ,  $\text{TiCl}_4$ , and  $\text{ZnCl}_2$  all produced heterogeneous mixtures of solid materials and viscous oils. The same reaction initiated by  $\text{FeCl}_3$  or sulfuric acid produced soft solids. Anhydrous  $\text{SnCl}_4$  afforded a hard, brittle solid that appeared to have a darker layer on the bottom. A solution of  $\text{BCl}_3$  in  $\text{CH}_2\text{Cl}_2$  (1M) produced only a dark-brown, free-flowing oil. On the other hand, BFE produced rigid plastics and appears to be the best initiator employed in this study.

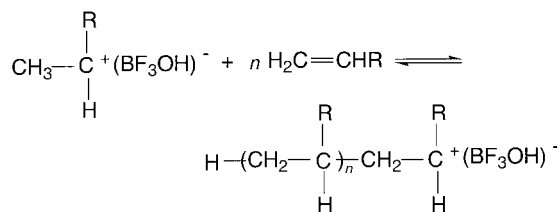
### Mechanism of BFE-Initiated Cationic Copolymerization

The BFE-initiated cationic polymerization of simple alkenes is well understood.<sup>26–28</sup> The initiation and propagation mechanisms are shown in Figure 3. The initiation process occurs in two steps. The BFE first reacts with a small amount of wa-

#### Initiation:



#### Propagation:



**Figure 3** The mechanism of cationic polymerization of simple alkenes.

ter that may be present in the reaction mixture to produce the hydrate complex. The boron trifluoride hydrate then reacts with the alkene to produce the initiator–coinitiator complex. Propagation then may occur through subsequent insertions of the alkene monomer into the initiator–coinitiator complex. Termination may occur at any time during the polymerization through chain transfer to a monomer, chain transfer to a polymer, or through spontaneous termination involving the donation of a proton from the propagating ion pair to the counterion regenerating the boron trifluoride hydrate and producing a double bond in the polymer.

The BFE-initiated homopolymerization or copolymerization of NFO or CFO with alkene comonomers is assumed to follow a similar cationic mechanism. The initiation processes may be similar to those mentioned above. However, the polyunsaturation of the NFO and CFO, plus the presence of several different alkene comonomers in these reactions, may complicate the chain propagation mechanisms. The homopolymerization of the NFO or CFO occurs by repetitive attack by an electrophilic carbocation on the  $\pi$  systems of the fatty acid ester molecules. From the standpoint of the structures in Figure 2, the fatty acid ethyl esters may not be sufficiently nucleophilic to support extensive chain propagation or steric hindrance of the long ethyl ester molecules may inhibit the chain propagation of  $\sim\text{M}_{12+}$  after cationic initiation ( $\text{M}_1$  represents a molecule of NFO or CFO).<sup>26</sup> Thus, simple homopolymerization of the NFO or CFO results in only low molecular weight viscous oils in most cases. The introduction of small alkene comonomers ( $\text{M}_2$ ) not only increases the nucleophilicity of the reactants, but also reduces the steric hindrance by generating  $\sim\text{M}_1\text{M}_{2+}$  species during chain propagation, which results in much higher molecular weight solid polymers.

Due to the multiple functional groups in the fish oils and the alkene comonomers, the polymers formed by cationic copolymerization are expected to be thermosets. The curing of the thermosets through a cationic mechanism may involve several steps. Copolymerization is also initiated by BFE by the formation and linear growth of chains that soon begin to branch and then crosslink. As the reaction proceeds, the increase in molecular weight accelerates, and eventually several chains become linked together into a network of infinite molecular weight, which corresponds to the gel point, an irreversible trans-

formation from a viscous liquid to an elastic gel or rubber. The polymers lose their ability to flow and are not readily processable beyond this point.

Gelation does not necessarily inhibit the curing process. In other words, the reaction rate may remain almost unchanged after the gel point. Vitrification of the growing networks follows when the continuously increasing glass-transition temperature ( $T_g$ ) of the growing network becomes coincidental with the cure temperature (i.e.,  $T_g = T_{\text{cure}} = T_{\text{room}}$ ). In the glassy state there is usually a significant decrease in the reaction rate as the reaction becomes diffusion controlled. In order to obtain fully cured networks, the materials are subsequently postcured at 60°C for 24 h and 110°C for 48 h.

### Cationic Copolymerization of NFO or CFO with Alkenes

#### *NFO-DVB-NBD-DCP Systems*

The gelation of the cationic copolymerization was measured by approximating the time it took for the liquid reactants to reach a certain high viscosity (i.e., elastic gel). The homopolymerization of NFO initiated by BFE resulted in viscous oils, and they did not gel at all at room temperature and above.

The addition of alkene comonomers, such as DVB, NBD, and DCP, obviously facilitated gelation of the NFO system. The gel times varies from 1 min to a few hours at room temperature, depending on the stoichiometry and specific alkene comonomer employed. For cationic copolymerization the gelation occurred at approximately 20% conversion, which was much lower than the 60–80% of condensation copolymerization systems.<sup>29</sup> The final products were obtained after three vitrification steps at different temperatures and were thus composed of fully cured networks.

The NFO readily polymerized with DVB in the presence of BFE to form soft to hard thermosets, depending on the amount of DVB employed. Polymerization reactions with 1, 2, or 5% BFE and 5–30% DVB were conducted and the mass recoveries for all of the reactions producing solid materials were nearly quantitative. When 5% BFE was used, 10% DVB was required to produce a soft material. As the amount of DVB was increased, the products became harder. If the amount of BFE used in the reaction was reduced to 1–2%, 15% DVB was required to produce a soft, solid material. When the DVB content was

greater than 20%, the resulting polymers were hard materials with plastic characteristics.

The BFE-initiated reaction with NFO, DVB, and NBD also produced hard plastics with appropriate stoichiometries. A small amount of the alkene comonomers resulted in the production of viscous oils. Typical hard plastics were produced from reactions with 20% DVB and 10% NBD. DVB and DCP were also simultaneously copolymerized with NFO to produce thermosets. Similarly, hard plastics were prepared using 20% DVB and 10% DCP. However, attempts to produce solid materials by polymerizing just the NFO and DCP or NBD were unsuccessful. In both cases only dark, viscous oils were produced, no matter how much of the alkene comonomer was used in the reaction.

#### *CFO-DVB-NBD-DCP Systems*

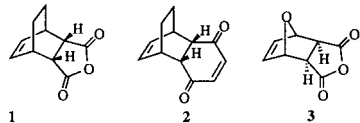
Conjugated NFO (CFO) is more reactive than the regular NFO. As a result, simple homopolymerization of the CFO results in a soft, solid material. Its gel time reaches more than 72 h at room temperature. As expected, the gel times from its copolymerization with various alkene comonomers decreased significantly and the reaction rates appeared to be similar to those of the above NFO systems.

The CFO reacts with DVB in the presence of BFE to produce very hard thermosets after three postcuring steps. A hard, pressure-resistant thermoset was produced using only 5% DVB, 94% CFO, and 1% BFE. The products became more rigid as the amount of DVB additive was increased from 5 to 30%. Hard plastics were produced by polymerizing the CFO with 30% DVB using 1, 2, or 5% BFE.

Copolymerization of the CFO with DVB and NBD also produced hard plastics. Very hard thermosets were prepared using 20% DVB, 10% NBD, and 1, 2, or 5% BFE. Like the NFO systems, copolymerization of CFO with DVB and DCP also substantially improved the rigidity of the resulting thermosets.

Because CFO is more reactive than the NFO, its copolymerization with alkene comonomers was quite different in some cases. The reaction of NFO with 5% DVB, 5% NBD, and 5% BFE produced only a soft gel, but the same reaction with the CFO produced a hard thermoset with 96% overall mass recovery. The reaction of 85% NFO, 5% DVB, 5% DCP, and 5% BFE produced a viscous oil; however, the same reaction produced a

**Table II** Alkene Comonomers Used for Cationic Copolymerization with NFO or CFO

Entry	Comonomers	Examples	Products
1	Furfural	60–70% NFO + 5–10% furfural + 20–25% DVB + 5% BFE	Hard thermosets
2	<i>p</i> -Benzoquinone	60–70% NFO + 10–15% <i>p</i> -benzoquinone + 10–25% DVB + 5% BFE	Hard thermosets
3	<i>p</i> -Mentha-1,8-diene	65% NFO + 10% <i>p</i> -mentha-1,8-diene + 20% DVB + 5% BFE 65% CFO + 10% <i>p</i> -mentha-1,8-diene + 20% DVB + 5% BFE	Hard thermosets
4	Furan	65–70% NFO + 10–15% furan + 15% DVB + 5% BFE	Hard thermosets
5		65% CFO + 10% <b>1</b> , <b>2</b> , or <b>3</b> + 20% DVB + 5% BFE 65% CFO + 30% <b>1</b> , <b>2</b> , or <b>3</b> + 5% BFE	Hard thermoset Soft polymer
6	Maleic anhydride	65 CFO + 30% maleic anhydride + 5% BFE 65% NFO + 10–20% maleic anhydride + 10–20% DVB + 5% BFE	Rubbery material Rigid thermosets
7	Vinyl acetate	75% CFO + 15% vinyl acetate + 5% DVB + 5% BFE 75% CFO + 20% vinyl acetate + 5% BFE	Hard thermoset Soft polymer

hard pressure-resistant thermoset when CFO was used. Although the native NFO failed to produce solid thermosets when polymerized with DCP in the presence of BFE, the CFO produced a soft, solid material when it was reacted with 5% DCP and 5% BFE. Increasing the amounts of DCP used in these reactions improved the rigidity of the polymers. A soft, rubbery copolymer could also be produced by reacting the CFO with 10% NBD and 5% BFE. However, increasing the amount of NBD used in the reaction resulted in the production of viscous oils. In general, thermosets prepared from CFO appeared to be harder than the materials produced by the same reactions with the NFO.

#### Other Alkene Comonomers

Table II shows that many other alkene comonomers, such as furfural, *p*-benzoquinone, *p*-mentha-1,8-diene, furan, Diels–Alder adducts **1–3**, maleic anhydride, and vinyl acetate, were also examined in the BFE-initiated copolymerization. Copolymerization of these alkene comonomers with NFO or CFO generated soft to hard polymers in the presence of DVB, NBD, or DCP. However, without the DVB, NBD, or DCP comonomers, solid polymers could not be obtained by

copolymerizing NFO or CFO with any of the following comonomers: Diels–Alder adducts **1** and **2**, *p*-mentha-1,8-diene, methyl acrylate, vinylidene chloride, methyl crotonate, isoprene, dimethyl acetylenedicarboxylate, diallyl phthalate, myrcene, phenol, linalool, furfural, 2-allylphenol, 1,2-dimethoxybenzene, or bisphenol A.

Interestingly, the copolymerization of acrolein and the CFO using catalytic BFE resulted in a violent exothermic reaction that could not be slowed, even by cooling the reactants to 0°C. The addition of DVB to the acrolein-CFO system also produced an immediate exothermic reaction upon the addition of BFE.

#### Characteristics of NFO and CFO Bulk Polymers

##### Structure of Bulk Polymers

The yields of the bulk polymers were found to be essentially quantitative. Table III gives the elemental analysis results of some NFO and CFO bulk polymers. Apparently, the elemental compositions of the bulk polymers were very close to the results calculated from the reactants. It followed that all of the NFO (or CFO) and alkene comonomers were present in the resulting bulk polymers.

The structure of the bulk polymers was studied by Soxhlet extraction with CH<sub>2</sub>Cl<sub>2</sub> or THF as the

**Table III Elemental Analysis of Bulk Polymers**

Entry	Polymers	Theoretical Results		Calculated Results	
		C	H	C	H
1	NFO65-DVB10-DCP20-BFE5	80.8	10.3	78.0	10.2
2	CFO65-DVB30-BFE5	80.0	9.8	79.0	9.7
3	CFO94-DVB5-BFE1	78.2	10.8	79.7	10.8
4	CFO65-DVB10-NBD20-BFE5	79.8	10.1	78.3	10.0

refluxing solvents. Table IV shows that 25–47% of the soluble materials were extracted from the NFO bulk polymers and 10–34% of the soluble materials were extracted from the CFO bulk polymers by  $\text{CH}_2\text{Cl}_2$  or THF. In most cases, the remaining insoluble materials accounted for more than 70% of the total mass of the bulk NFO and CFO thermosets. The CFO bulk polymers possessed much higher amounts of insoluble materials than the NFO bulk polymers. We found that the  $\text{CH}_2\text{Cl}_2$  extraction results were very similar to the THF results, which indicated that  $\text{CH}_2\text{Cl}_2$  and THF were both good solvents for the soluble materials present in the NFO and CFO bulk polymers.

Figure 4 contains the  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR spectra of the soluble materials extracted from the bulk polymer CFO65-DVB30-BFE5. The results showed that the extracted materials had a structure similar to that of the CFO, except that a substantial number of the  $\text{C}=\text{C}$  bonds disappeared. The  $^1\text{H}$ -NMR spectrum showed very few vinylic hydrogens ( $\delta = 5.2\text{--}5.5$  ppm), and the  $^{13}\text{C}$ -NMR spectrum showed a limited number of  $\text{sp}^2$

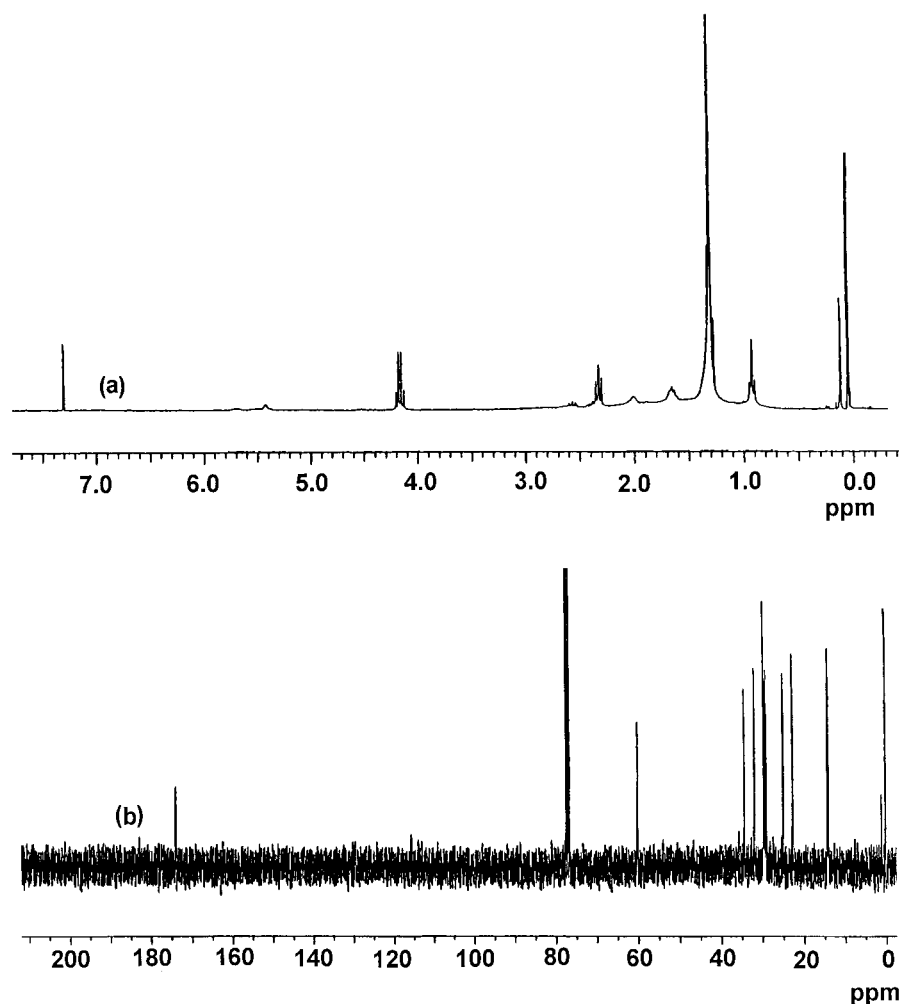
carbons in the alkene region ( $\delta = 120\text{--}140$  ppm). It followed that the extracted soluble materials were unreacted free oils with very few  $\text{C}=\text{C}$  bonds. However, their molecular weights could not be measured by gel permeation chromatography or mass spectrometry.

The insoluble materials were expected to be highly crosslinked polymeric materials. The THF insoluble materials resulting from the extraction of the CFO65-DCP30-BFE5 copolymer were examined using solid-state CP MAS  $^{13}\text{C}$ -NMR spectroscopy (Fig. 5). The spectrum clearly showed the presence of ester carbonyls ( $\delta = 165\text{--}175$  ppm) and carbon–carbon double bonds ( $\delta = 120\text{--}140$  ppm). The THF insoluble materials from the CFO65-DVB30-BFE5 copolymer were also examined by solid-state CP MAS  $^{13}\text{C}$ -NMR. The data confirmed the presence of ester carbonyls and carbon–carbon double bonds, although the double bonds present were largely due to the incorporation of DVB into the copolymer backbone.

The preceding discussion implied that the NFO and CFO bulk polymers were composed of cross-

**Table IV Soxhlet Extraction Results for NFO and CFO Polymers**

Entry	Polymer	Bulk Polymer Extraction (% Insoluble – % Soluble)	
		$\text{CH}_2\text{Cl}_2$	THF
1	NFO65-DVB30-BFE5	58–37	65–32
2	NFO65-DVB10-NBD20-BFE5	73–25	60–38
3	NFO69-DVB10-NBD20-BFE1	55–45	58–42
4	NFO65-DVB10-DCP20-BFE5	52–47	49–47
5	CFO65-DVB30-BFE5	77–19	78–19
6	CFO85-DVB10-BFE5	74–22	72–26
7	CFO94-DVB5-BFE1	64–31	64–34
8	CFO65-DVB10-NBD20-BFE5	79–17	75–23
9	CFO50-DVB15-NBD30-BFE5	86–10	84–16
10	CFO89-DVB5-NBD5-BFE1	68–26	66–33
11	CFO65-DVB10-DCP20-BFE5	75–17	74–23



**Figure 4** The  $^1\text{H}$ - (spectrum a) and  $^{13}\text{C}$ -NMR (spectrum b) spectra of the soluble materials extracted from the CFO65-DCP30-BFE5 bulk polymer.

linked polymer networks with a certain amount of unreacted free oil. However, the fish oil segments incorporated into the crosslinked networks still had some unreacted C=C bonds present.

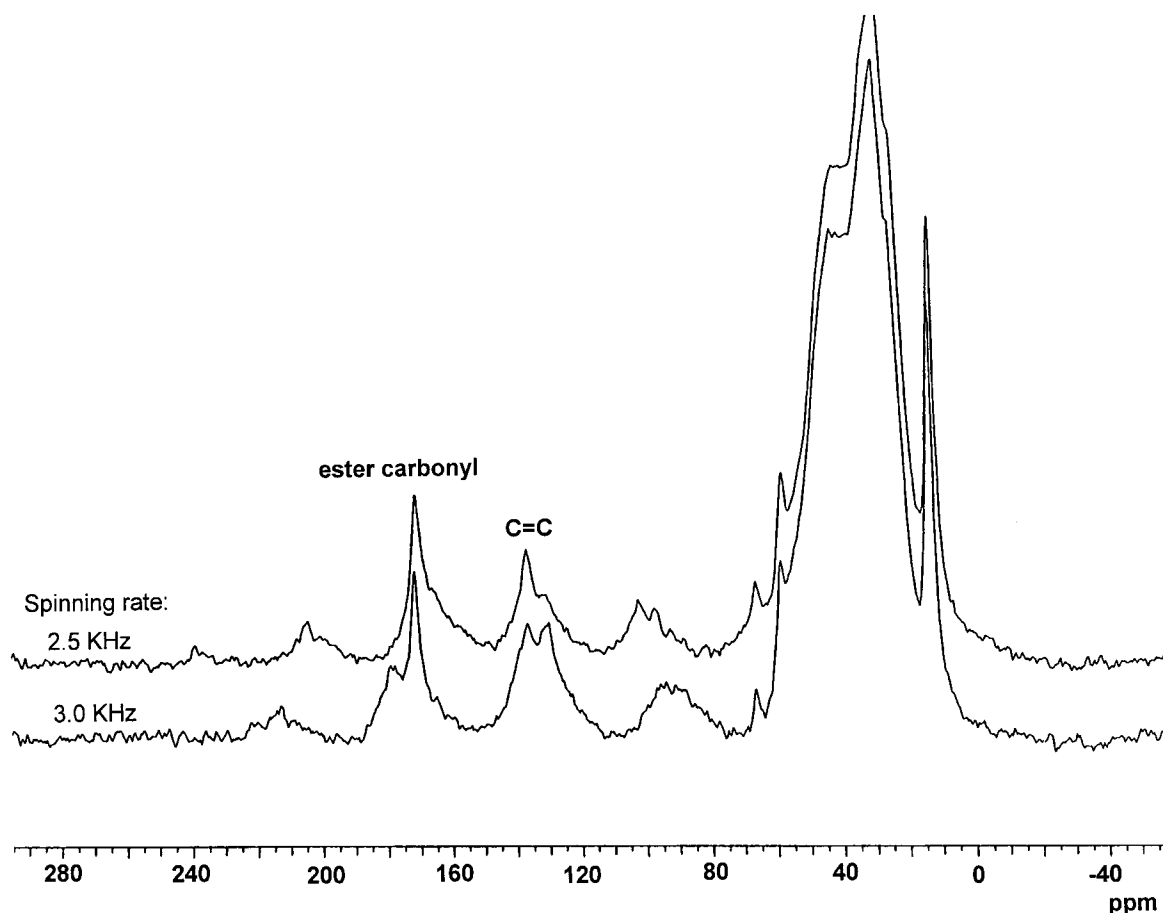
#### **Thermal Characterization of Bulk Polymers**

Figure 6 shows the derivatives of the TGA curves of the bulk polymer CFO50-DVB15-NBD30-BFE5, plus its soluble and insoluble materials after extraction. Three characteristic weight loss steps were observed for the bulk polymer at approximately 200–400, 400–600, and 600–800°C in an air atmosphere. In the first step, the bulk polymer lost approximately 10% of its weight. The second decomposition was the major process and corresponded to nearly 70% weight loss, which started at 400°C and ended at around 600°C. The third step afforded about a 20% weight loss at

600–800°C. By comparing the TGA derivatives of the soluble and insoluble materials in Figure 6, it became clear that the first decomposition of the bulk polymer corresponded to the major decomposition process of the free oils, the second decomposition corresponded to degradation and char formation of the crosslinked polymer network, and the third decomposition corresponded to oxidation of the char residues in air. In a nitrogen atmosphere the third decomposition did not appear.

We obtained TGA data for some NFO bulk polymers (Table V, entries 1–4). The temperatures corresponding to 10% weight loss were obtained under nitrogen and air atmospheres for each bulk polymer. The percentage of polymer mass remaining at 400°C was also noted for each thermoset. Generally, most of the NFO polymers





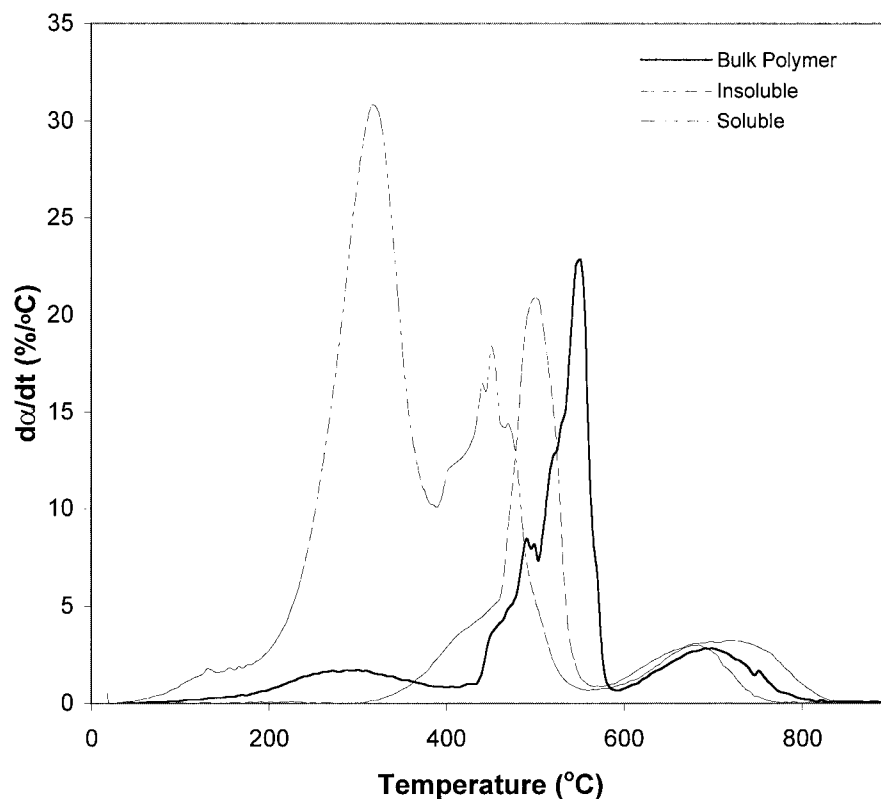
**Figure 5** The solid-state  $^{13}\text{C}$ -NMR spectrum of the insoluble materials remaining after extraction of the CFO65-DCP30-BFE5 bulk polymer.

lost 10% of their mass between 234 and 290°C. All of the thermosets still possessed 72–79% of their initial mass at 400°C. Specifically, when some DVB was replaced by NBD, the resulting polymer showed lower thermal stability (Table V, entries 1 and 2). When 1% initiator was used instead of 5%, the thermal stability of the resulting polymer increased slightly (Table V, entries 2 and 3). However, the NFO polymer with the highest thermal stability was obtained by using DVB plus DCP comonomers (Table V, entry 4). It is also noteworthy that the NFO thermosets had a slightly higher thermal stability in air than in nitrogen. Such behavior was unexpected.

Table V also shows the TGA results for the CFO bulk polymers under nitrogen and air atmospheres. Most of the CFO polymers appeared to lose 10% of their mass between 226 and 338°C, a temperature region similar to that of the NFO bulk polymers. Generally, the thermal stability of the CFO bulk polymers was also related to their

stoichiometries. Unlike the NFO bulk polymers, however, the thermal stability of the resulting polymers decreased when NBD or DCP replaced part of the DVB (Table V, entries 5, 8, and 11). When more comonomers were used, the thermal stability of the resulting CFO polymer was substantially increased (Table V, entries 8 and 9). For example, the polymer CFO50-DVB15-NBD30-BFE5 lost 10% of its mass at approximately 334–338°C in both nitrogen and air atmospheres. The percentage of polymer mass remaining at 400°C reached as high as 87% (Table V, entry 9).

One might expect that the thermal stability would be, to some extent, related to the rigidity of the materials. However, in some cases there appeared to be little correlation. For instance, the CFO65-DVB10-NBD20-BFE5 polymer (Table V, entry 8) was much harder than the NFO65-DVB10-DCP20-BFE5 polymer (Table V, entry 4), but the softer polymer lost 10% of its mass under nitrogen at 285°C while the harder polymer lost



**Figure 6** Derivative TGA curves of the CFO50-DVB15-NBD30-BFE5 bulk polymer, its soluble materials, and the remaining insoluble materials after extraction.

10% of its mass at 244°C. The thermal stability of the polymers did not seem to be a function of the catalyst load used in the reaction either. For example, NFO69-DVB10-NBD20-BFE1 lost 10% of its weight at 249°C and NFO65-DVB10-NBD20-

BFE5 lost 10% of its weight at 234°C. Thus, the polymer produced using a smaller catalyst load was slightly more thermally stable. The inconsistency was probably due to the decomposition mechanism. Generally, the 10% weight loss cor-

**Table V** TGA Results for NFO and CFO Polymers and Their Extracted Materials

Entry	Polymer	Bulk Polymer TGA				Extracted Polymer TGA	
		10% $T_{N_2}$ (°C)	% Mass $N_2$ (400°C)	10% $T_{air}$ (°C)	% Mass Air (400°C)	10% $T_{N_2} - T_{air}$ (°C)	
						$CH_2Cl_2$	THF
1	NFO65-DVB30-BFE5	265	72	269	74	445–436	456–442
2	NFO65-DVB10-NBD20-BFE5	234	74	234	76	426–410	432–396
3	NFO69-DVB10-NBD20-BFE1	249	76	254	79	431–428	418–410
4	NFO65-DVB10-DCP20-BFE5	285	77	290	79	445–448	433–392
5	CFO65-DVB30-BFE5	239	76	271	69	438–405	436–389
6	CFO85-DVB10-BFE5	284	75	283	76	418–382	422–387
7	CFO94-DVB5-BFE1	238	65	245	67	423–393	427–396
8	CFO65-DVB10-NBD20-BFE5	244	79	231	80	401–413	373–358
9	CFO50-DVB15-NBD30-BFE5	334	87	338	87	402–394	386–371
10	CFO89-DVB5-NBD5-BFE1	249	67	246	70	432–424	427–415
11	CFO65-DVB10-DCP20-BFE5	226	72	239	76	438–417	438–421

responded to the first decomposition step (i.e., evaporation and degradation of the free oils in the bulk polymers). This step was actually composed of two distinct processes: diffusion of the oil from the bulk to the surface and subsequent degradation or evaporation. Because the diffusion process was expected to be determined by many factors, it was difficult to correlate the polymer rigidity or stoichiometry with the thermal properties.

DSC was also used to examine the thermal properties of the NFO and CFO bulk polymers. A very broad shoulder was observed at approximately 100°C, corresponding to the glass transitions of the thermosets. No postcuring behavior was detected, which indicated that the glass-transition temperatures were representative of fully cured thermosets.

#### ***Thermal Characterization of Extracted Insoluble Materials***

Table V lists the TGA data for the CH<sub>2</sub>Cl<sub>2</sub> and THF insoluble materials obtained after extraction of the NFO and CFO thermosets. Compared with the bulk polymers, the insoluble materials showed remarkable thermal stability. All of the insoluble materials examined lost 10% of their mass at temperatures above 400°C.

The compositions of the bulk polymers seemed to have no direct effect on the thermal stability of the insoluble materials. For instance, contrary to expectations, the CH<sub>2</sub>Cl<sub>2</sub> and THF insoluble materials from the CFO94-DVB5-BFE1 copolymer (Table V, entry 7) were more thermally stable than the CH<sub>2</sub>Cl<sub>2</sub> and THF insoluble materials resulting from the CFO65-DVB10-NBD20-BFE5 copolymer (Table V, entry 8). The insoluble materials did not contain low molecular weight substances. Thus, their thermal stability was expected to be determined by the nature of the crosslink network structure, which, at this stage, was difficult to characterize.

However, unlike the bulk polymers, all of the insoluble materials appeared to be more thermally stable in nitrogen than in air. The highest thermal stability recorded for any of the insoluble materials was a 10% weight loss at 456°C under a nitrogen atmosphere for the THF insoluble materials from the NFO65-DVB30-BFE5 copolymer (Table V, entry 1).

#### **CONCLUSION**

The NFO and CFO proved to be cationically polymerizable monomers. Homopolymerization of

NFO or CFO only afforded low molecular weight viscous oils in most cases. Copolymerization of NFO or CFO with a wide range of alkene comonomers resulted in viable solid plastics within appropriate stoichiometries. Among a number of Lewis acids, BFE proved to be the most effective initiator for copolymerization. Comonomers such as DVB, NBD, and DCP were necessary for copolymerization to afford viable thermoset plastics. The gelation process of the copolymerization was largely dependent upon the stoichiometry, the type of comonomer employed, and the reaction conditions. Following postcuring at elevated temperatures, the BFE-initiated copolymerization afforded solid materials ranging from soft rubbers to rigid plastics, which appeared to be fully cured thermosets.

The resulting NFO and CFO bulk polymers were composed of a crosslinked polymer network and a certain amount of free oils. Generally, the CFO bulk materials possessed more crosslinked polymer than the NFO bulk materials. However, their thermal properties were similar to each other. The bulk polymers lost 10% of their weight at 230–330°C, and the percentage of polymer mass remaining at 400°C ranged from 65 to 87%. The insoluble materials remaining after extraction exhibited much higher thermal stability with 10% weight loss at 401–445°C.

We would like to thank the Iowa Soybean Promotion Board for funding this research and Dr. Valerie V. Sheares for helpful suggestions and the use of her thermal analysis instrumentation.

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