

# Crosslinking and Decomposition Reactions of Epoxide Functionalized Polynorbornene. Part I. FTIR and Thermogravimetric Analysis

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**ABSTRACT:** The miniaturization of microelectronic devices has created a demand for new low-dielectric-constant materials to be used as insulating layers between metal interconnects. In this study, a functionalized polynorbornene consisting of a copolymer of decyl norbornene and epoxide norbornene has been investigated as a low-temperature curing dielectric. Polynorbornenes possess properties that are attractive for microelectronics packaging; however, films of these polymers must be crosslinked in order to obtain the solvent resistance and low solvent swelling necessary for multilayer applications. Crosslinking of these materials was achieved by acid-catalyzed cationic crosslinking

of epoxide side groups. The reactions that occurred during higher temperature curing of epoxy functionalized norbornene films were studied using Fourier transform infrared (FTIR) spectroscopy and thermogravimetric analysis. Epoxide crosslinking and epoxide decomposition reactions were identified and studied as a function of temperature and time. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 89: 568–577, 2003

**Key words:** polynorbornenes; FTIR; TGA; crosslinking; curing; microelectronics

## INTRODUCTION

Current trends in the semiconductor industry point to continually decreasing component size leading to increasing processor speeds, as seen in the appearance of multi-gigahertz processors and high-performance portable palmtop computers. The use of low-dielectric-constant insulating materials in these products decreases the propagation delay experienced by a signal as it is carried through metal interconnection by reducing the capacitive coupling between metal lines.<sup>1–3</sup> Polymers based on a polynorbornene backbone have been explored for this use.<sup>4,5</sup> Dielectrics based on a polynorbornene backbone are attractive because they possess a low dielectric constant ( $\epsilon_r \sim 2.2\text{--}3.0$ ) and low moisture uptake (0.1%–1.0% by weight). The specific reactive and material properties of the polymer film can be tailored to suit specific applications by attaching side groups to a polynorbornene backbone. Similar studies<sup>5</sup> have focused on the use of triethoxysilyl and alkyl side groups to improve adhesive properties and mechanical properties, respectively. This article investigates reactions that occur during the cure of a photosensitive polymer with a polynorbornene back-

bone functionalized with decyl and epoxy side groups. Epoxy side groups have been selected to provide a mechanism for crosslinking. Decyl side groups have been selected to improve the mechanical properties in films with high levels of crosslinking. An iodonium salt is used as a photoacid generator to initiate crosslinking reactions.

The cationic crosslinking of epoxide groups initiated by acid generators has been studied for a variety of applications.<sup>6–9</sup> The reaction sequence, shown in Figure 1, is proposed as the mechanism by which a crosslinking network is formed. In this figure, R and R' represent to the remainder of the hydrocarbon chain. Four distinct reaction steps occur: initiation, activation, propagation, and termination. Initiation occurs when an onium salt ( $\text{Ph}_2\text{I}^+\text{X}^-$ ) decomposes to form a protic acid (HX). This can occur by either photolysis or by thermal decomposition.<sup>10</sup> The resultant protic acid consists of a proton paired with the bulky anion part of the onium salt. This acid can attack the unbonded electron pairs of the oxygen in an epoxide ring, resulting in the ring's opening and the formation of a hydroxyl group and a carbocation. The opening of the epoxide ring creates an active center where either a propagation or termination reaction can occur. Propagation occurs when the carbocation attacks the strained oxygen of a neighboring epoxide group to form a crosslink. Theoretically, the resultant carbocation can continue to propagate until all epox-

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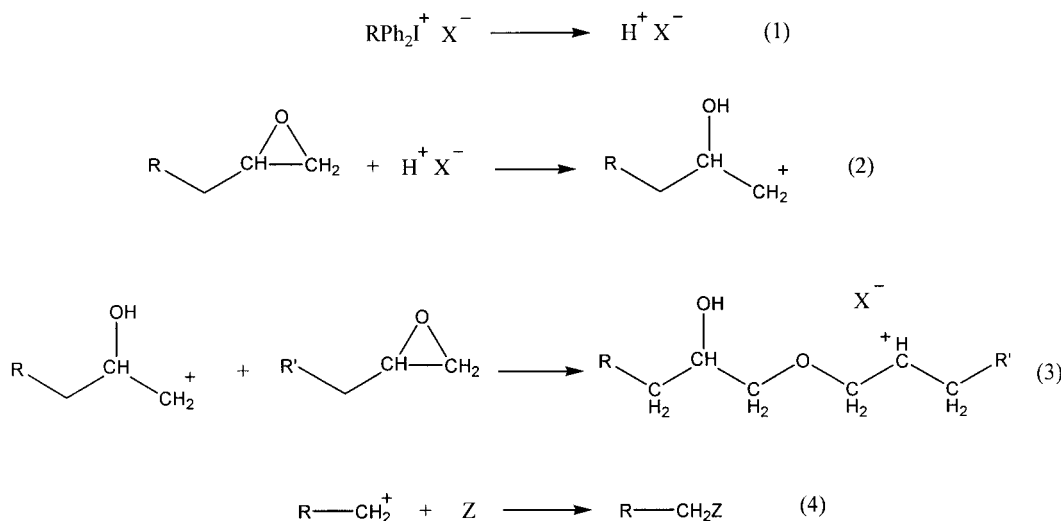


Figure 1 Proposed crosslinking mechanism.

ide rings are consumed; however, steric and mobility limitations make this unlikely. A carbocation at any stage can be terminated by the presence of a nucleophilic impurity such as water (defined as Z).<sup>7,8</sup> It is not necessary for a termination mechanism to exist, as a carbocation can exist for indefinite periods of time with the anion pair nearby to balance the charge.<sup>7</sup> In this article, the reactions that occur during the epoxide ring opening and crosslinking are studied by Fourier transform infrared spectroscopy (FTIR) and thermogravimetric analysis (TGA).

## EXPERIMENTAL

The norbornene copolymer used in this study was obtained from Promerus LLC (Brecksville, OH). The general structure of a copolymer of decyl norbornene and epoxide norbornene is shown in Figure 2. The polymer is a random copolymer where each of the seven member norbornene rings on the backbone is functionalized with either decyl or epoxide side groups. For convenience, the mole ratio of decyl to epoxide side groups is used to describe the specific copolymer in question. For example, a 40/60 DecNB/EpNB corresponds to a polymer where 40 mol % of the norbornene backbone units possess decyl side groups and the remaining 60 mol % of backbone units have epoxide side groups. The polymers were prepared as a 20 wt % solution in mesitylene. An iodonium salt was used as the photoacid generator (represented as  $\text{RPh}_2\text{I}^+\text{X}^-$  in Fig. 1). This onium salt is sensitized to UV exposure at 365 nm by the addition of a sensitizer.

FTIR is used to track the chemical changes that occur in the film. FTIR scans were collected in transmission mode on potassium bromide (KBr) substrates using a Nicolet Magna IR 560 equipped with a pro-

grammable heated *in situ* cure cell. Samples were prepared by coating each KBr substrate with polymer solution and heating to 100°C to drive off solvent in a convection oven. For each measurement, 64 scans at a resolution of 4  $\text{cm}^{-1}$  were averaged.

Thermogravimetric analysis (TGA) was used to track changes in weight on thermal excursions in nitrogen atmospheres. The weight percent as a function of temperature and time was measured using a Seiko TG/DTA 320 thermogravimetric analyzer. Samples were prepared for analysis by placing a drop of polymer solution in a TGA sample pan and evaporating solvent in a vacuum oven. TGA experiments were performed in both dynamic (5°C/min) and isothermal modes.

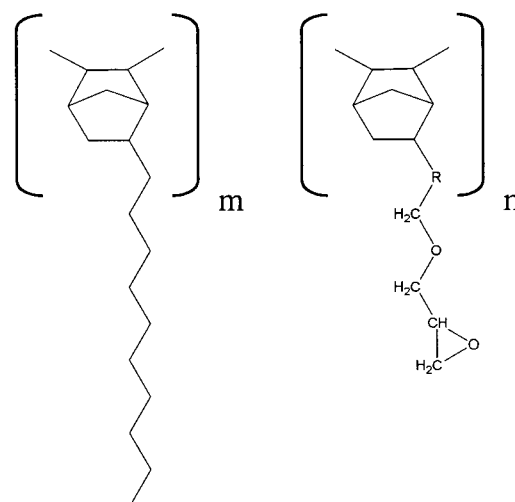


Figure 2 General structure for a copolymer of decyl norbornene and epoxide norbornene (decyl : epoxide, m : n).

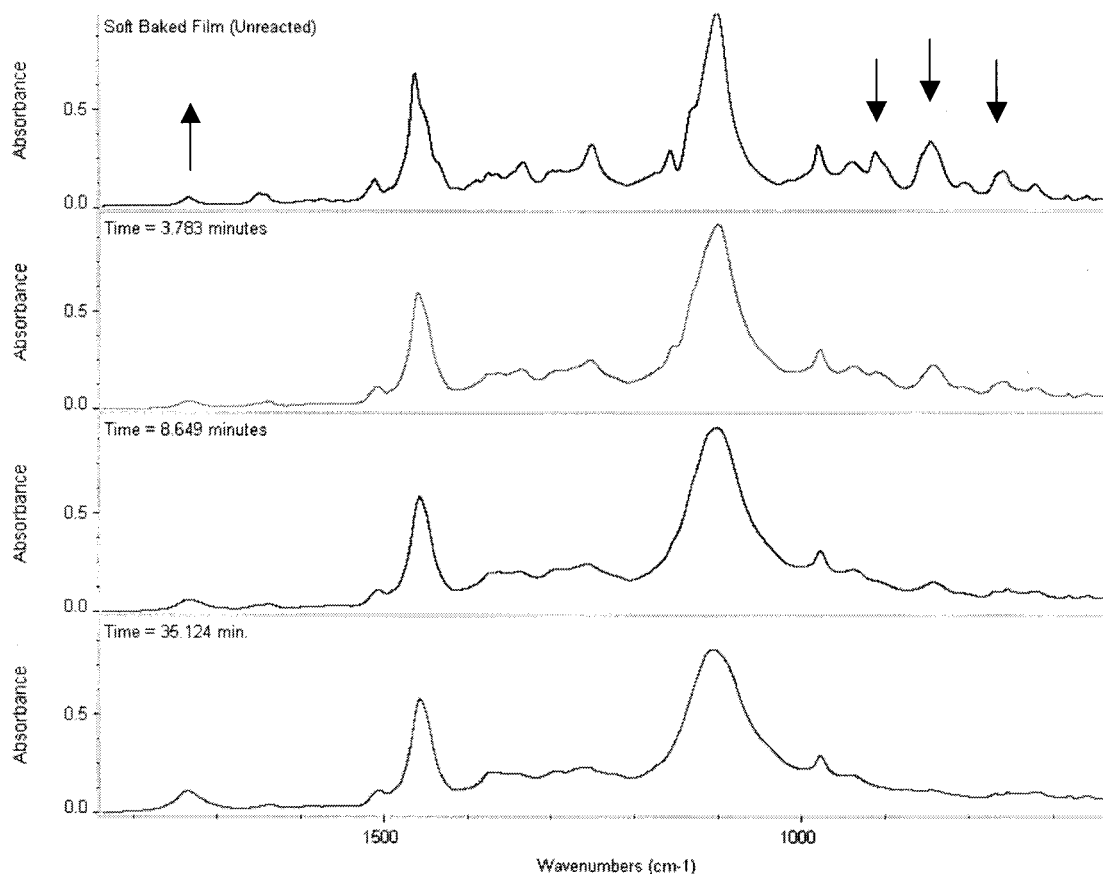


Figure 3 Changes in the infrared spectra of 40/60 DecNB/EpNB in the range from 1800 to 700  $\text{cm}^{-1}$  at 200°C.

## RESULTS

### FTIR Analysis

The infrared spectra in the region from 1800 to 700  $\text{cm}^{-1}$  and 3700 to 3200  $\text{cm}^{-1}$  are shown in Figures 3 and 4. The spectra shown were acquired after exposure to 500  $\text{mJ}/\text{cm}^2$  on a sample of 40/60 DecNB/EpNB formulated with photoacid generator and sensitizer as this sample is cured in an heated cell at 200°C. In these figures, the change in spectra can be seen as the reaction proceeds with time.

From these infrared spectra the following observations can be made. First, three peaks corresponding to asymmetric and symmetric epoxide ring stretches were observed at 913, 844, and 760  $\text{cm}^{-1}$ . These peaks decreased with time as the cure proceeded to 200°C, which indicated the opening of the epoxide rings. Second, the formation of a C—O—C crosslink ( $\sim 1100 \text{ cm}^{-1}$ ) cannot be verified by FTIR because the strong absorbance peak of the ether group initially present in the epoxide side group interferes with the detection of new ether linkages. Third, the broad absorbance in the range from 3600 to 3300  $\text{cm}^{-1}$  is characteristic of hydrogen-bonded OH groups. Hydroxyl groups are formed in the acid-catalyzed epoxy ring opening reaction to form a propagating cation. It is important to

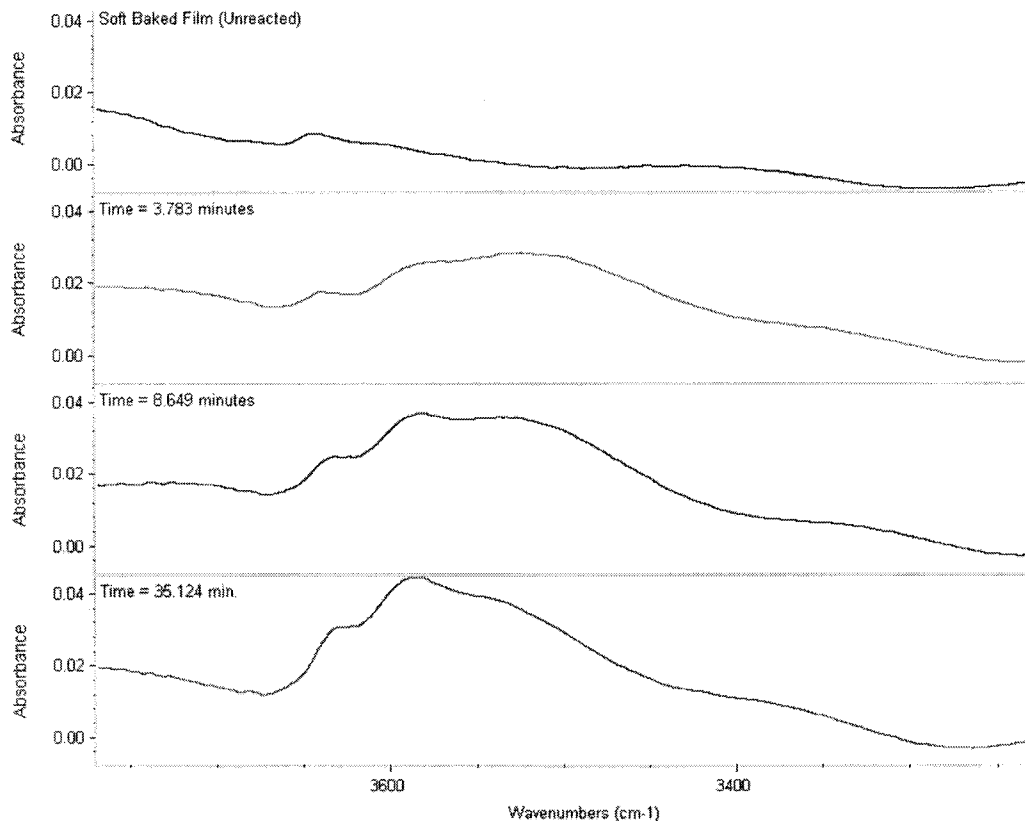
recognize that the only source of OH groups is the reaction of generated acid with an unreacted epoxide ring (Step 2 of the mechanism shown in Fig. 1). Fourth, the peak absorbance at 1737  $\text{cm}^{-1}$ , corresponding to the production of carbonyl groups, increases during cure. The production of carbonyl groups is unexpected and will be discussed in more detail later in this article.

Chemical changes in the film can be quantified by tracking changes in the intensity of IR peaks (height or area) corresponding to specific groups. By using the peak at 1460  $\text{cm}^{-1}$  (asymmetric aliphatic carbon-hydrogen distortions) as an internal spectral reference, the infrared spectra at different stages of cure and from different samples can be compared. In general, the infrared absorbance corresponding to any group can be represented relative to the internal reference by

$$\text{normalized absorbance} = \frac{h_{\text{peak}}}{h_{1460}} \text{ or } \frac{A_{\text{peak}}}{h_{1460}}$$

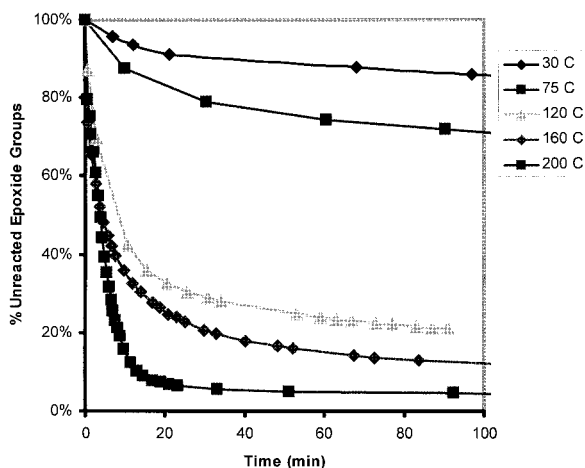
where  $h_{1460}$  is the baseline corrected peak height at 1460  $\text{cm}^{-1}$ . Either the peak height ( $h_{\text{peak}}$ ) or area ( $A_{\text{peak}}$ ) can be used to quantify changes in absorbance.

The disappearance of epoxide rings (844  $\text{cm}^{-1}$ ) monitored as a function of cure temperature for a



**Figure 4** Changes in the infrared spectra of 40/60 DecNB/EpNB in the range from 3600 to 3300  $\text{cm}^{-1}$  as a function of cure time at 200°C.

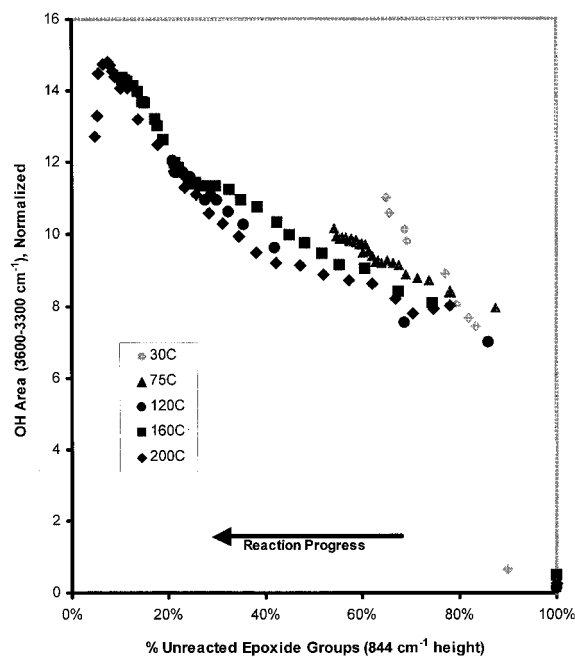
sample of 40/60 DecNB/EpNB is shown in Figure 5. The peak height is used to measure the epoxide content because both the peak height and area decrease proportionally on cure. The initial rate and final extent of the epoxy ring opening reaction is greater at higher cure temperatures. This may be due to an increase in reaction rate due to kinetic effects as described by the



**Figure 5** Epoxide remaining ( $844 \text{ cm}^{-1}$ ) versus cure time for a sample 40/60 DecNB/EpNB cured at 30, 75, 120, 160, and 200°C.

Arrhenius relationship. This phenomena may also be due to mass transport effects associated with an increased diffusion coefficient of reactive groups (i.e., generated acid or opened epoxide rings) at greater temperatures. It is important to recognize that all reactions occur at temperatures less than the glass transition temperature of the polymer film ( $T_g > 200^\circ\text{C}$ ). Reactions of polymers that proceed at temperatures less than the glass transition temperature are often diffusion controlled. Additionally, any photoacid that is not decomposed during exposure to UV radiation can be thermally decomposed to generate acid.<sup>10</sup> For the specific onium salt used, the thermal decomposition temperature has been determined to be 130°C using differential scanning calorimetry. Thermally generated acid will react with unopened rings forming carbocations, but does not necessarily directly assist in the propagation reactions that lead to crosslinks.

Figure 6 shows the change in absorbance corresponding to OH groups ( $3600\text{--}3300 \text{ cm}^{-1}$ ) as a function of the number of epoxide rings remaining ( $844 \text{ cm}^{-1}$ ) for a sample of 40/60 DecNB/EpNB. The area under the absorption peak in this region is an appropriate measure of OH content, because these groups are characterized by broad absorption in this region due to extensive hydrogen bonding. The production



**Figure 6** Hydroxyl content ( $3600\text{--}3300\text{ cm}^{-1}$  area) versus epoxide remaining ( $844\text{ cm}^{-1}$  height) for a sample of 40/60 DecNB/EpNB cured at 30, 75, 120, 160, and  $200^\circ\text{C}$ .

of OH groups can only occur as a result of acid attack on an epoxide ring. Three distinct phases can be identified. First, there is a significant increase in the OH area after exposure, corresponding to the opening of epoxide rings that are in immediate proximity to the photo generated acid (Step 2 in Fig. 1). It is interesting to note that more than half of the OH groups formed are produced in the ring opening of only the first 15% to 20% of the epoxide groups. In the second phase, the OH peak area gradually increases as the next 80% of epoxide rings are opened. Both acid catalysis and carbocation attack (Steps 2 and 3 in Fig. 1) contribute to ring opening of the epoxide rings in this phase. Samples cured at 30 and  $75^\circ\text{C}$  show only the initial increase in OH content suggesting that the mechanism for epoxide ring opening in these samples is primarily acid attack and significant levels of crosslinking do not occur. Appreciable crosslinking formation, therefore, requires curing at higher temperatures.

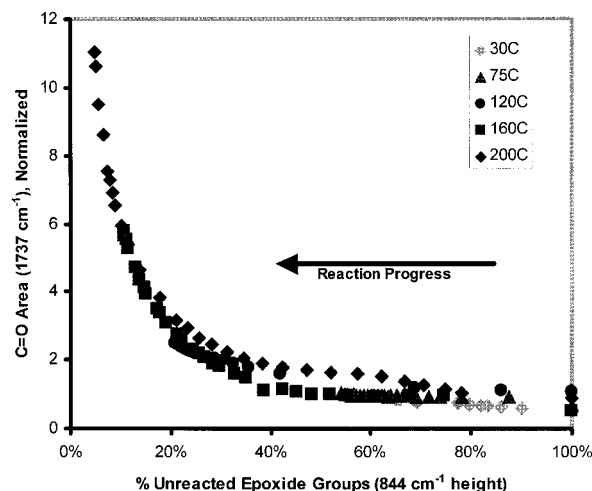
In the third phase, the OH stretch peak area decreases slightly upon consumption of the final 5% of epoxide groups. The third phase exists only for samples cured at  $200^\circ\text{C}$  (Fig. 6). Alcohol/epoxide etherification reactions have been proposed by some researchers to be responsible for a decrease in overall OH content at higher temperatures.<sup>11,12</sup> These reactions, however, require higher content of acid species and occur at temperatures greater than  $300^\circ\text{C}$ . An alternate mechanism for this occurrence will be proposed in the next section.

A plot of the normalized peak area corresponding to carbonyl groups ( $1737\text{ cm}^{-1}$ ) as a function of the num-

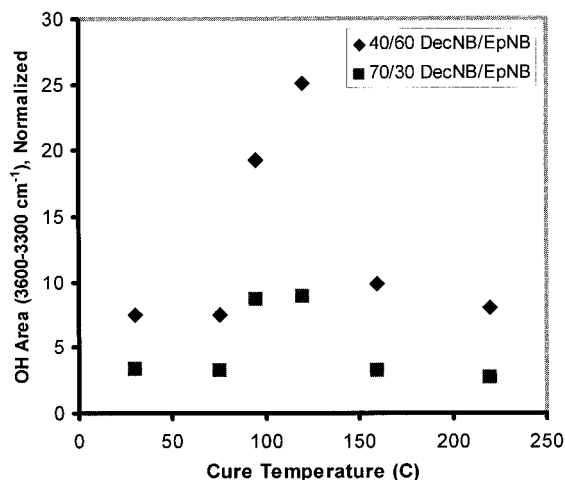
ber of epoxide groups remaining ( $844\text{ cm}^{-1}$ ) is shown in Figure 7 for samples of 40/60 DecNB/EpNB. Carbonyl groups are present in small molar quantities as attached groups in the sensitizer/photoacid additives. The carbonyl peak area remains low for the consumption of the first 60% of epoxide. At higher conversions of epoxide (lower epoxide remaining), the carbonyl peak area increases rapidly. For temperatures greater than  $160^\circ\text{C}$ , the carbonyl peak area increases with significant consumption of epoxide. This data suggest that the production of carbonyl groups is not strongly related to the opening of the epoxide ring. Additionally, carbonyl groups are not expected to be products of the crosslinking mechanism as shown in Figure 1.

For the next set of experiments, samples of fully formulated 40/60 and 70/30 DecNB/EpNB are prepared on KBr crystals for FTIR transmission analysis. Each sample is soft baked, exposed to  $500\text{ mJ/cm}^2$ , and cured for 10 h at cure temperature. This cure time is selected to be very long, with the intent to drive all chemical reactions to completion.

The OH content ( $3600\text{--}3300\text{ cm}^{-1}$ ) plotted as function of cure temperature is shown in Figure 8. Regardless of cure temperature, samples of 40/60 DecNB/EpNB have approximately twice as many hydroxyl groups produced as samples of 70/30 DecNB/EpNB. This is expected because these samples have twice the number of epoxide groups attached to the polynorbornene backbone. The hydroxyl content in the film increases with cure temperature for temperatures up to  $120^\circ\text{C}$ , presumably due to the acid-catalyzed ring opening. For cure temperatures at  $160^\circ\text{C}$  or greater, the hydroxyl content is significantly lower. The data presented previously for *in situ* cure monitoring showed a slight lowering of OH content at  $200^\circ\text{C}$  for a



**Figure 7** Carbonyl content ( $1737\text{ cm}^{-1}$  area) versus epoxide remaining ( $844\text{ cm}^{-1}$  height) for a sample 40/60 DecNB/EpNB cured at 30, 75, 120, 160, and  $200^\circ\text{C}$ .



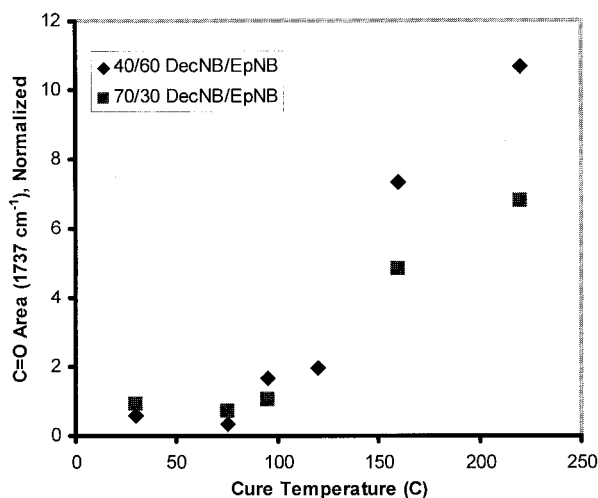
**Figure 8** Hydroxyl content ( $3600\text{--}3300\text{ cm}^{-1}$  area) versus cure temperature for samples cured for 10 h.

shorter cure time. This suggests that the mechanism for loss of hydroxyl groups appears to be a slow reaction that requires significant time at temperature to proceed.

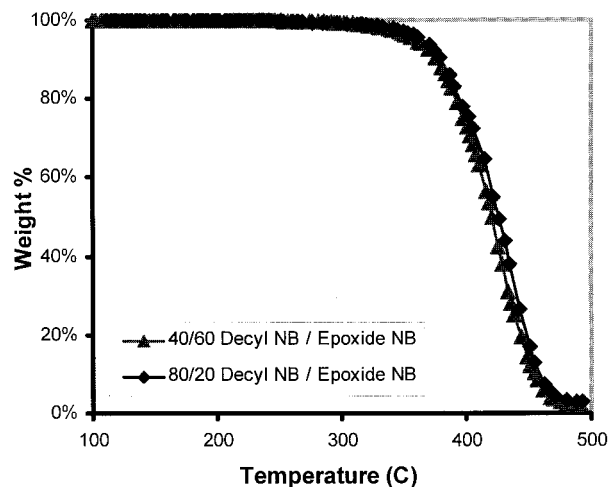
The carbonyl content ( $1737\text{ cm}^{-1}$ ) plotted as a function of cure temperature is shown in Figure 9. For longer cure times (10 h), the carbonyl content remains low until cure temperatures greater than or equal to  $160^\circ\text{C}$ . Additionally, samples of 40/60 DecNB/EpNB produce approximately twice as many carbonyl species as samples of 70/30 DecNB/EpNB, suggesting that the production of carbonyl groups is linked to the level of epoxide groups present in the system.

### Thermogravimetric analysis (TGA)

Figure 10 shows weight loss as a function of temperature for dry samples of 40/60 and 80/20 DecNB/EpNB/



**Figure 9** Carbonyl content ( $1737\text{ cm}^{-1}$  area) versus cure temperature for samples cured for 10 h.

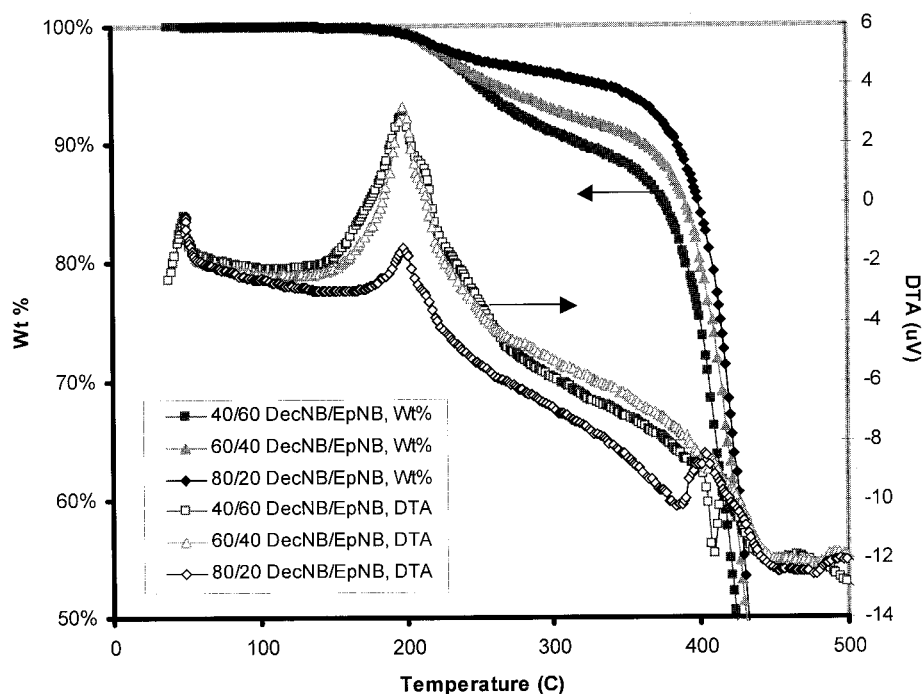


**Figure 10** Weight percent versus temperature as samples of unformulated 40/60 and 80/20 DecNB/EpNB are ramped at  $5^\circ\text{C}/\text{min}$ .

EpNB ramped at  $5^\circ\text{C}/\text{min}$  to  $500^\circ\text{C}$  as measured in the TGA. At this ramp rate, the polymer loses 1% and 5% of its weight at  $310$  and  $360^\circ\text{C}$ , respectively. This weight loss appears to be independent of side group and photo-additives and is first detected at  $260^\circ\text{C}$ . Wedlake<sup>13</sup> has observed similar phenomena in his kinetic study of the decomposition of alkyl functionalized polynorbornenes. These results support the hypothesis that subtle changes in the side groups attached to the backbone of the polymer do not drastically affect the temperature at which decomposition of the polynorbornene backbone occurs.

Dry polymer films of 40/60, 60/40, and 80/20 DecNB/EpNB are prepared from polymer solutions formulated with photoacid and sensitizer additives. The dynamic TGA scan for a formulated sample is considerably different than that for unformulated samples. Figure 11 shows the weight loss as a function of temperature for samples of fully formulated 40/60, 60/40, and 80/20 DecNB/EpNB ramped at  $5^\circ\text{C}/\text{min}$  to  $500^\circ\text{C}$ . These samples are exposed to  $500\text{ mJ}/\text{cm}^2$  before loading into the TGA chamber. The weight loss occurs in two stages: an initial weight loss followed by a greater final weight loss. The second drop in weight is likely not attributed to the epoxy functionality but rather due to backbone effects.

The first decrease in weight occurs at  $160^\circ\text{C}$ , regardless of the ratio of decyl to epoxide side groups. This weight loss is not observed for unformulated samples and is therefore a direct consequence of the presence of photoacid and sensitizer additives. It is important to note that the total weight of additives in fully formulated (photoacid and sensitizer) polymer samples is less than 6% of the total polymer weight. A weight loss of greater than 10% is observed for a sample of 40/60 DecNB/EpNB. It is therefore unlikely that volatilization of additives are responsible for the first-



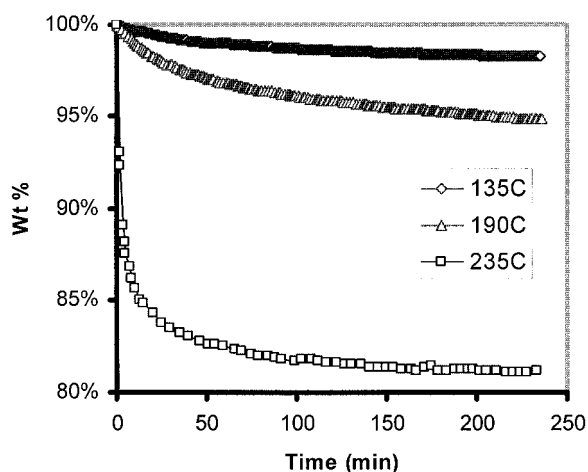
**Figure 11** Weight percent and DTA signal versus temperature for samples of formulated 40/60, 60/40, and 80/20 DecNB/EpNB at a ramp rate of 5°C/min.

stage weight loss. Additionally, the weight loss correlates directly to the level of epoxy attached to the backbone, suggesting that volatile species associated with the epoxide groups are responsible for this weight loss.

Figure 11 also shows the differential thermal analysis (DTA) signal as a function of temperature, corresponding to the energy transfer to or from the sample during the experiment. At least two overlapping exothermic peaks are observed to occur over this temperature scan, indicating there is most likely more than one reaction occurring. The DTA exotherm observed occurs over a time period of 45 min over a temperature range of 140 to 250°C. FTIR analysis indicates that all epoxide rings are consumed at these temperatures in a matter of a few minutes. This implies that although the weight loss is associated with the presence of epoxide groups, it is not a result of ring opening or crosslinking reactions.

Isothermal TGA experiments are performed on samples of dry polymer films of 40/60 DecNB/EpNB to determine the weight loss on cure at 135, 190, and 235°C. Fully formulated samples are exposed and loaded into the TGA chamber. The sample is ramped at 100°C per min to the appropriate hold temperature for 240 min. Figure 12 shows the isothermal weight loss at each temperature. There is approximately a 1.5% weight loss for the sample held for 240 min at 135°C. This weight loss is most likely due to loss of absorbed moisture or residual solvent. Studies have shown that an epoxide functionalized norbornene

polymer film can absorb moisture up to 1% by weight.<sup>4</sup> A sample held at 190°C exhibited a weight loss of approximately 6% after 240 min. It appears as though the weight has not stabilized and will continue to decrease. A sample held at 235°C for 240 min loses approximately 18% of its initial mass. This sample was intentionally held at a temperature below the backbone decomposition temperature (~260°C) to isolate the weight loss that occurs during the first drop in weight.



**Figure 12** Weight loss at temperature for a sample of formulated 40/60 DecNB/EpNB at 135, 190, and 235°C for 240 min.

## DISCUSSION

The results from infrared can be summarized as follows. First, the epoxide-ring opening reaction can be derived by a photo or thermally generated acid followed by heating. Second, the epoxide ring opening reaction can be monitored by the disappearance of the absorbance peak at  $844\text{ cm}^{-1}$ . The rate of ring opening increases with cure temperature, possibly due to an increased diffusive mobility of generated acid and opened epoxide rings. Third, an increase in the OH area from  $3600$  to  $3300\text{ cm}^{-1}$  confirms that the epoxide rings are opened by the generated acid. The OH area increases with further reaction, but decreases for samples cured at temperatures greater than  $160^\circ\text{C}$  for longer cure times. Finally, the carbonyl content in the polymer film increases substantially at temperatures greater than  $160^\circ\text{C}$  and is proportional to the epoxide content initially in the film, but independent of the level of epoxide ring opening. Both the decrease in OH groups and the production of carbonyl groups are not predicted by the proposed crosslinking mechanism (Fig. 1).

The results from thermogravimetric analysis can also be summarized. First, an unformulated DecNB/EpNB copolymer (without photoacid generator and sensitizer) will start to exhibit weight loss at  $260^\circ\text{C}$ , regardless of copolymer ratio. This weight loss is most likely due to backbone decomposition. Second, a sample of fully formulated DecNB/EpNB polymer (containing photoacid generator and sensitizer) exhibits a two-stage weight loss. The first weight loss starting at  $160^\circ\text{C}$  is followed by a larger weight loss starting at  $260^\circ\text{C}$  that is attributed to backbone decomposition. Third, the weight loss in the first stage of weight loss starting at  $160^\circ\text{C}$  is directly related to the level of epoxide groups present in the polymer system. Finally, the rate of weight loss at  $T > 160^\circ\text{C}$  is very slow, on the order of hours, suggesting that the process is linked to the diffusion of generated acid to reactive sites. Comparison of the time scale of this weight loss and the DTA signal to the time scale of the epoxide ring opening (monitored by FTIR) suggests that although the weight loss is related to the epoxide groups, it is not related to the epoxide ring opening or crosslinking reactions.

From these results, it appears that at least two separate reaction mechanisms are occurring. The first reaction is the desired epoxide ring opening and crosslinking reactions initiated by a thermally generated or photo-generated acid. This reaction can occur at all temperatures after the acid species is generated. At temperatures greater than  $160^\circ\text{C}$ , a decomposition reaction occurs resulting in weight loss. This decomposition reaction is characterized by three attributes. First, the weight loss is directly proportional to the level of epoxide groups attached to the polynor-

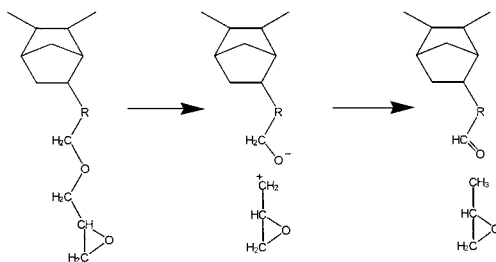
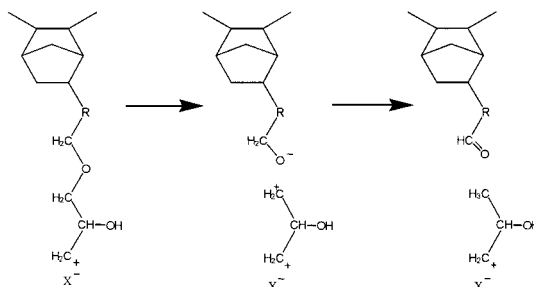
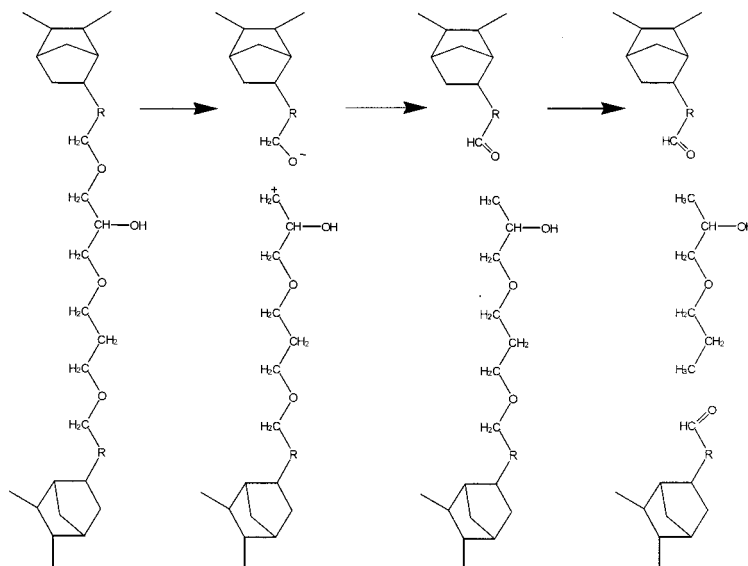
bornene backbone. Second, a significant amount of carbonyl groups is produced. Finally, there is a decrease in OH groups that accompanies the increase in carbonyl groups.

The decomposition mechanism shown in Figure 13 is proposed in order to explain the phenomena associated with this secondary reaction. The ether moiety in the epoxide structure may be catalyzed by the presence of acid to cleave. Subsequent isomerization of the produced oxygen anion will result in a carbonyl group. This mechanism results in the loss of the complete epoxide structure. At this point, the epoxide group can exist in either unreacted, opened, or crosslinked forms. The ring opening reaction kinetics is fast in comparison to the decomposition reaction. Therefore, the majority of epoxide rings are opened before the decomposition reactions can significantly occur. The proposed decomposition mechanism will result in a decrease in hydroxyl groups if the epoxide rings are open during decomposition. Infrared analysis cannot distinguish between reacted epoxide rings and rings lost by cleavage at the ether group. A decrease in the FTIR absorbance peaks of both epoxide rings and hydroxyl groups will occur as these epoxide groups are volatilized. Additionally, the number of crosslinks in the system will be reduced if in fact these epoxide groups are decomposing and volatilizing.

The weight loss associated with the loss of epoxide groups is calculated and shown in Table I. This number represents the maximum weight loss possible if all epoxide groups undergo cleavage at the ether group. The weight loss due to the decomposition is estimated by extrapolating the weight loss from the dynamic TGA shown in Figure 11 that occurs during the first stage of decomposition. Additionally, a polymer of 40/60 DecNB/EpNB experiences a weight loss of 18% during an isothermal hold at  $235^\circ\text{C}$ . The weight loss predicted by the decomposition mechanism closely matches the values determined by extrapolation of dynamic data and the isothermal weight loss at  $235^\circ\text{C}$ . This provides further support for the proposed decomposition mechanism.

A similar thermal degradation mechanism has been proposed for bisphenol. A diglycidyl ether (BADGE) type epoxies.<sup>14-16</sup> The ether group in the glycidyl ether (epoxide) structure has been identified as the most likely location for scission. In unformulated samples, the primary volatile products during decomposition were identified as acrolein, acetone, and allyl alcohol. These three compounds are structural isomers of the volatile product proposed in Figure 13 for uncrosslinked epoxide rings. Grassie, Guy, and Tennent<sup>14,15</sup> also proposed a similar mechanism for crosslinked epoxies that resulted in loss of the linkage. For both crosslinked and uncrosslinked systems, the remaining ether group is converted into a carbonyl containing aldehyde group. The isomerization of these



**Unreacted Epoxide Group:****Opened Epoxide Group:****Crosslinked Epoxide Groups:**

**Figure 13** Proposed decomposition mechanism for the formation of carbonyl groups and loss of hydroxyl groups.

groups to form aldehyde groups has been proposed by others as well.<sup>17,18</sup>

**SUMMARY**

The results presented in this work suggest two independent reactions occur during the thermal cure of a copolymer of decyl norbornene and epoxide norbornene initiated by a photoacid generator. On exposure to UV radiation or heating to temperatures greater than 130°C, the generation of acid will pro-

**TABLE I**  
Predicted Weight Loss Based on  
Decomposition Mechanism

DecNB/EpNB ratio	Predicted weight loss	Extrapolation of dynamic TGA data	Isothermal weight loss at 235°C
40/60	17%	15%	18%
60/40	11%	11%	—
80/20	6%	6%	—

mote epoxide ring opening reactions and subsequent formation of crosslinks. This reaction is likely to be limited by the diffusive mobility of reactive species (generated acid and opened epoxide rings) to unopened epoxide rings. At temperatures greater than 160°C, a decomposition mechanism occurs by which cleavage occurs at the ether linkage, resulting in a complete loss of the epoxide group. This mechanism is slow compared to the epoxide ring opening and crosslinking reactions.

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