

# A Dynamic FT-IR Method for Determining the Curing Temperature Ranges of an Acetylene-Terminated Polyisoimide Prepolymer

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## SYNOPSIS

A dynamic FT-IR method was used to determine the individual curing temperature ranges of the isoimide-imide isomerization and crosslinking reactions of an acetylene-terminated polyisoimide prepolymer. The individual curing temperature ranges of these two types of chemical reactions for the polyisoimide system using differential scanning calorimetry (DSC) were totally overlapped. Using dynamic FT-IR spectroscopy, the curing temperature ranges of the isomerization and crosslinking reactions were clearly separated. The isomerization reaction began at lower temperatures than the crosslinking reaction and was complete when only half of the crosslinking reaction had occurred. The temperature width,  $\Delta T_{1/2}$ , was twice as great for the crosslinking reaction compared with the isomerization reaction. Activation energies from dynamic FT-IR spectroscopy can be obtained for the two separate reactions, however, for the reactions considered here, the activation energies were similar, 26 kcal/mol for the isomerization reaction and 23 kcal/mol for the crosslinking reaction.

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## INTRODUCTION

The acetylene-terminated polyisoimide prepolymer (Thermid IP-600™) derived from 3,3', 4,4'-benzophenonetetracarboxylic dianhydride, 3-ethynylaniline, and 1,3-bis(3-aminophenoxy) is a multifunctional group monomer in which there are four isoimide groups in the middle of the monomer backbone and two acetylene-terminal groups (see Fig. 1). The isoimide groups are introduced to improve solubility in common organic solvents compared with the acetylene-terminated polyimide isomer (Thermid MC-600™). Acetylene-terminated groups are used to polymerize the monomers into three-dimensional void-free networks that have excellent thermal-oxidation stability and high solvent resistance.<sup>1</sup> Two types of chemical reactions occur on the system during the thermal curing process—the isoimide-imide isomerization, and the crosslinking

reactions—both of which are thermally initiated (see Fig. 1).

Differential scanning calorimetry (DSC) is conventionally used to determine thermal properties of materials, including the curing temperature ranges of polymerization reactions. DSC thermal analysis under dynamic conditions reflects endothermic or exothermic changes occurring in the system under investigation.<sup>2-5</sup> Dynamic DSC has often been employed as a precursor to isothermal studies,<sup>3</sup> especially for samples with multiple exotherms, unreliable baselines, etc. The acetylene-terminated polyisoimide prepolymer, Thermid IP-600™, has been investigated using IR,<sup>6,7</sup> NMR,<sup>8</sup> and dynamic DSC,<sup>9</sup> but the individual curing temperature ranges for the isoimide-imide isomerization and crosslinking reactions of Thermid IP-600™ have not been reported, because they were totally overlapped on the DSC curves.

The isoimide-imide isomerization is an intramolecular rearrangement that involves local, short-range segmental motions, while the crosslinking reaction is an intermolecular reaction involving long-range segmental motions of the chain that bring the

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chain ends into close proximity for reaction. The isoimide-imide conversion is believed to obey first-order kinetics in solution, and, thus, in the solid state, but the reaction mechanism for the crosslinking reaction is still not completely understood.<sup>6</sup> It is anticipated that there are different curing temperature ranges for these two reactions, although the individual temperature ranges were not separated by conventional thermal analysis techniques.

In order to determine individual curing temperature ranges of the isoimide-imide isomerization and crosslinking reactions, a rapid-scan dynamic FT-IR method was developed in which the two reactions were continuously monitored as the sample was heated at constant rate. Isothermal kinetic data have been obtained on FT-IR spectrometers using their fast scan capability<sup>9,10</sup> and GC-IR software.<sup>11</sup> Recently, Snyder and Sheen developed a method for collecting kinetic data from dynamic FT-IR experiments,<sup>12,13</sup> and utilized this method for monitoring the high-temperature imidization of poly(amic) acids. In the present article, we used the dynamic FT-IR method with a common kinetics program to monitor the two separate reactions occurring during the thermal curing process of the acetylene-terminated polyisoimide prepolymer Thermid IP-600<sup>™</sup> and to determine the individual curing temperature ranges of the isoimide-imide isomerization and crosslinking reactions. The results were compared with dynamic FT-IR and dynamic DSC data obtained for a model compound, IP-6001, in which only the isomerization reaction occurred and for Thermid MC-600<sup>™</sup>, in which only the crosslinking reaction occurred. The advantage of the dynamic FT-IR method is that the individual absorbances of the multifunctional groups of Thermid IP-600<sup>™</sup> in the mid-ir region can be separated and so represent "windows" for the different chemical reactions occurring during the thermal curing process. In our case, we selected the peak of the isoimide carbonyl group ( $1808\text{ cm}^{-1}$ ) to monitor the isoimide-imide isomerization and the peak of the acetylene-terminated group ( $3238\text{ cm}^{-1}$ ) to monitor the crosslinking reaction. These particular functional peaks can be monitored directly and simultaneously by FT-IR spectroscopy and then analyzed separately by computer program, even if the individual temperature ranges of the chemical reactions on one system are partially or totally overlapped.

## EXPERIMENTAL

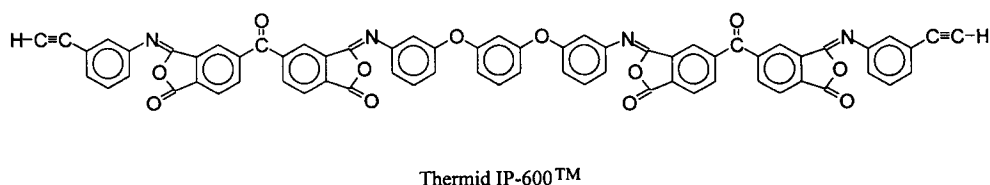
An acetylene-terminated polyisoimide prepolymer, Thermid IP-600<sup>™</sup> was commercially avail-

able from the National Starch & Chemicals Corporation, as was the imide prepolymer Thermid MC-600<sup>™</sup>. The aniline terminated polyisoimide, IP-6001 was available only for research purposes. The structure of these compound are shown in Figure 1. The samples in the powdered state were stored in the refrigerator before use. The "melting points" for the samples were obtained using a Thomas Hoover capillary melting point apparatus, with the results presented in Table I. Thermid IP-600<sup>™</sup> and IP-6001 were observed to flow, but Thermid MC-600<sup>™</sup> only changed color from yellow to slightly reddish at the transition.

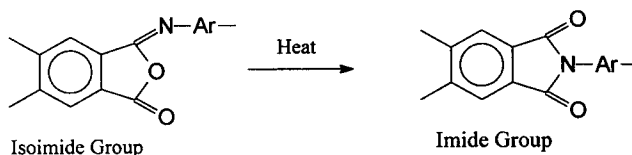
DSC experiments were performed on a Perkin-Elmer DSC-2 differential scanning calorimeter. Samples of about 2.0–4.0 mg were contained in aluminum sample pans with tightly sealed lids. The samples were heated at  $2.5^\circ\text{C}/\text{min}$ ,  $5^\circ\text{C}/\text{min}$ ,  $10^\circ\text{C}/\text{min}$ , and  $15^\circ\text{C}/\text{min}$  under a nitrogen purge of 20 psi. Temperature ranges for the thermal analysis runs were from  $50\text{--}450^\circ\text{C}$ , and dynamic data were collected between  $70\text{--}430^\circ\text{C}$ .

The samples used for FT-IR analysis were dissolved in tetrahydrofuran (THF) at a concentration of 10% w/w. The solutions were cast onto  $25 \times 4$  mm NaCl salt plates using a Headway Photo-Resistant spinner. The speed of the spinner was controlled at 2500 rpm and the samples were spun for 30 s in order to produce films sufficiently thin (ca  $5\ \mu\text{m}$ ) and uniform so that the initial IR absorbances were well within 0.4–0.6 absorbance units. The solvent was removed by placing the sample in a vacuum oven overnight at  $70\text{--}80^\circ\text{C}$ . Optical observation of the spun films showed a "corn cob" texture (which did not exhibit polarization properties) for IP-600<sup>™</sup>. No texture was observed for either Thermid MC-600<sup>™</sup> or IP-6001. The melting temperature range for the spun films was similar to that observed for the powdered samples.

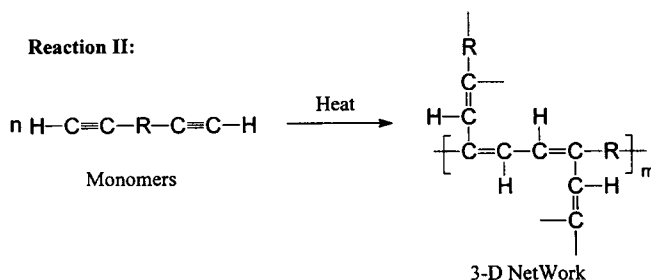
For the dynamic FT-IR experiments, the thermal curing process of the polyisoimide was carried out using a specially designed brass cell, which was heated using four 100 watt electric heaters. The outside of the high temperature cell was wrapped with 1/2 inch insulation. Samples were mounted in the center of the heated cell and the diameter of optical path was 12 cm. The samples were held on one NaCl plate rather than sandwiched between two salt plates, because water vapor interfered with the spectra in the latter arrangement. In the dynamic experiments, preheating the sample at lower temperatures did not eliminate water interference as the temperature was increased. Temperature control of better than  $\pm 1^\circ\text{C}$  was achieved using a CN-2041



Reaction I:



Reaction II:



**Figure 1** The molecular structure of the acetylene-terminated polyisoimide prepolymer, Thermid IP-600™, and chemical reactions occurring in Thermid IP-600™: (I) Isoimide-imide isomerization reaction; (II) Crosslinking reaction.

Omega programmable temperature controller with a K-type thermocouple. A wrapped ceramic tube temperature probe was inserted into the cell and touched the sample surface. There was a temperature difference of about 10°C between the copper heating block and the sample surface, which increased slightly with increasing temperature. In order to accurately determine heating rates and temperatures, the thermocouple attached to the sample surface was used to measure and control the temperature for the dynamic experiments, chosen to coincide with those of the DSC scans, i.e., 5°C/min, 10°C/min, and 15°C/min. The temperature range

at different heating rates was set from 110–380°C, and data was collected from 130–320°C to ensure linearity of the temperature ramp.

Dynamic FT-IR spectroscopy was performed using a Mattson Galaxy 2020 FT-IR instrument with a DTGS CsI detector and a ceramic filament source. Dynamic spectra were collected from 700–3600 cm<sup>-1</sup> in the mid-ir region at a spectral resolution of 4 cm<sup>-1</sup> (for 5°C/min ramp) or 8 cm<sup>-1</sup> (for the 10°C/min and 15°C/min ramp). An average of 12 scans were collected for each heating rate.

In the dynamic FT-IR method, the peak intensities of the functional groups are continuously

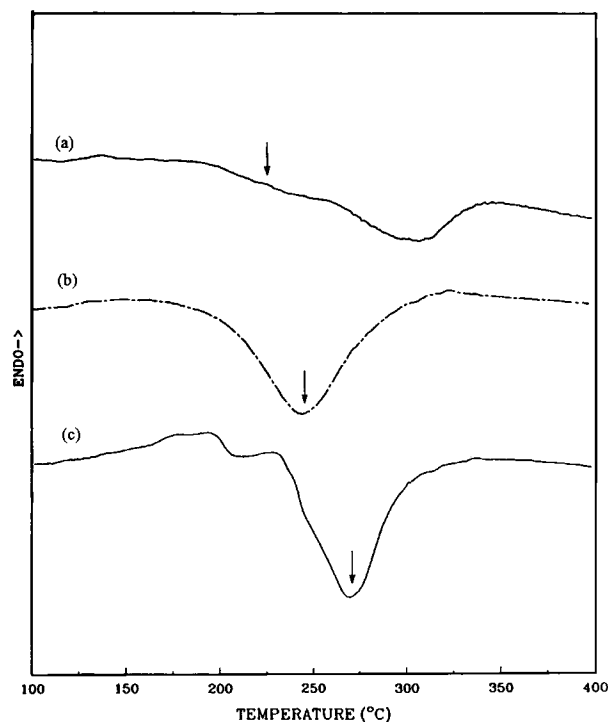
**Table I** “Melting” Temperature Ranges of Thermid IP-600™, IP-6001, and MC-600™

| Oligomers                | Thermid IP-600 | Model IP-6001 | Thermid MC-600         |
|--------------------------|----------------|---------------|------------------------|
| Bulk Sample <sup>a</sup> | 153–163°C      | 158–166°C     | 196–222°C <sup>c</sup> |
| Thin Film <sup>b</sup>   | 156–167°C      | —             | —                      |

<sup>a</sup> Using melting point apparatus.

<sup>b</sup> Using optical microscope.

<sup>c</sup> Only color change observed.



**Figure 2** DSC thermal analysis of (a) the model compound IP-6001 at a heating rate of 10°C/min, (b) Thermid IP-600™ at a heating rate of 10°C/min, (c) Thermid MC-600™ at a heating rate of 10°C/min.

monitored as a function of temperature during the thermal curing process. In general, the dynamic FT-IR method requires a rapid-scan, short data transformation process and a fast response detector. The optimum parameters of the FT-IR instrument depend on both the heating rate and the rate of the reaction. For the polyisoimide sample, we set the movable mirror of the instrument at the maximum speed of 2.0 cm/s and collected the data as interferograms without instantaneous transformation to absorbance spectra in order to minimize data processing time and thus collect as much data per unit time as possible.

Unlike the case of isothermal FT-IR data, where it is possible to reach constant background conditions, the temperature and humidity of the FT-IR chamber under dynamic conditions changes during the ramping sequence. In order to ensure that there was no background interference, it was necessary to collect the background and sample interferograms under identical thermal conditions. Thus, at each heating rate two dynamic scans were run, one with the sample and one with an empty cell for the background. The interferogram spectra were then converted into absorbance spectra using the corresponding backgrounds. Nearly 100 spectra of the

polyisoimide were collected at each heating rate in the temperature interval from 130 to 320°C in 38 min (5°C/min), 19 min (10°C/min), and 12.7 min (15°C/min).

## RESULTS AND DISCUSSION

In the study of acetylene-terminated polyisoimide prepolymers, the temperature range of the individual chemical reactions is important to elucidate the interrelationship between the isoimide-imide isomerization and crosslinking reactions occurring during the thermal curing process. It is important to know what temperatures have to be reached in order to ensure that the individual reactions go to completion. The individual temperature ranges are also useful in order to select the correct temperature ranges for obtaining kinetic parameters of the isomerization and crosslinking reactions of the polyisoimide under isothermal curing conditions.

All of the dynamic DSC thermograms of Thermid IP-600™ contained only one broad exothermic peak, as shown in Figure 2(b) for the 10°C/min run. This peak resulted from both chemical reactions occurring in the sample, the isoimide-imide isomerization, and the crosslinking reaction. Table II presents the data for the four heating rates giving: (1) the full temperature range of the reaction, determined by the temperature at which the thermogram deviated from baseline values; (2)  $T_{max}$ , the peak temperature of the thermogram; and (3)  $\Delta T_{1/2}$ , the full width at half height, which is another measure of the temperature range of the reactions. The data indicate that the two chemical reactions occurred during the same broad temperature range and, thus, the individual temperature ranges for the isomerization and crosslinking reaction could not be distinguished by DSC thermal analysis. With increasing heating rate,

**Table II** The Curing Temperature Range of the Isomerization and Crosslinking Reactions of Thermid IP-600™ at Different Heating Rates Obtained from the Dynamic DSC Method

| Heating Rate | Isomerization and crosslinking |           |                  |
|--------------|--------------------------------|-----------|------------------|
|              | Temperature Range              | $T_{max}$ | $\Delta T_{1/2}$ |
| 2.5°C/min    | 159–274°C                      | 215°C     | 62°C             |
| 5°C/min      | 164–286°C                      | 232°C     | 47°C             |
| 10°C/min     | 170–315°C                      | 243°C     | 52°C             |
| 15°C/min     | 182–319°C                      | 253°C     | 55°C             |

**Table III The Curing Temperature Range of the Crosslinking Reactions of Thermid MC-600™ at Different Heating Rates Obtained from the Dynamic DSC and FT-IR Methods**

| Heating Rate | Dynamic DSC |            |                  | Dynamic FT-IR |                   |                  |
|--------------|-------------|------------|------------------|---------------|-------------------|------------------|
|              | Temp. Range | $T_{\max}$ | $\Delta T_{1/2}$ | Temp. Range   | $T_{\text{flex}}$ | $\Delta T_{1/2}$ |
| 2.5°C/min    | 182–265°C   | 222°C      | 34°C             | —             | —                 | —                |
| 5°C/min      | 192–284°C   | 240°C      | 36°C             | 183–289°C     | 239°C             | 49°C             |
| 10°C/min     | 194–316°C   | 257°C      | 37°C             | 186–308°C     | 258°C             | 62°C             |
| 15°C/min     | 197–329°C   | 265°C      | 39°C             | —             | —                 | —                |

$T_{\max}$  increased. The heating rate dependence was expected because at slower heating rate, the samples were held longer at each temperature, so that each reaction proceeded to a greater extent.

For comparison, the DSC thermograms of a model compound, IP-6001, which is the same as Thermid IP-600™ except that the end groups are aniline rather than acetylene, and Thermid MC-600™, which is identical to Thermid IP-600™ but has imide rather than isoimide linkages, were obtained. Figure 2(a) and (c) show the DSC traces of these compounds at a heating rate of 10°C/min, and Tables III and IV give the data for all the heating rates. The arrows in Figure 2 show the exotherms associated with the isomerization reaction for IP-6001 [Fig. 2(a)], the crosslinking reaction for MC-600™ [Fig. 2(c)], and both reactions for IP-600™ [Fig. 2(b)]. The lower temperature exotherm for IP-6001 was assigned to the isoimide-imide conversion based on FTIR data presented below. The figure demonstrates that the isomerization reaction precedes the crosslinking reaction and that when both reactions occur, the maximum in the exotherm occurs at a temperature between the two.

Although flow was observed optically for the IP-6001 and IP-600™ samples beginning at about 155°C, there is no evidence for melting endotherms in the DSC traces. As discussed later, FTIR data

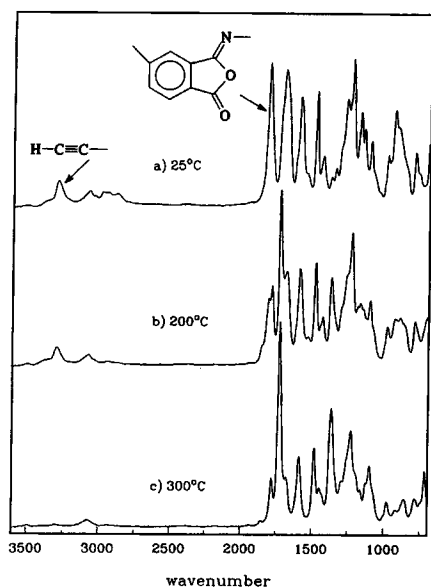
shows that the exothermic isoimide-imide conversion also begins at this temperature, perhaps masking the melting endotherm. The thermogram of Thermid MC-600™ [Fig. 2(c)] showed an endothermic peak starting at around 168°C followed by smaller and then larger exotherms at around 193 and 230°C, respectively. This behavior was observed for all heating rates. A possible explanation is that there is a melting endotherm beginning at 168°C immediately followed by the crosslinking exotherm. This results in partial compensation in the calorimetric data and explains why no visible flow is observed optically. Table III lists the temperature range for the exothermic transition as spanning both the small and large peaks, but gives  $\Delta T_{1/2}$  and  $T_{\max}$  for only the larger peak.

The thermogram of IP-6001 [Fig. 2(a)] contained two peaks that partially overlapped. The higher temperature exotherm has been tentatively assigned to the crystallization of the imide that is forming. This assignment was made based on the observations that (1) mass spectral analysis at a temperature of 250°C for 1 h showed no evolution of low molecular weight by-product resulting from side reactions or degradation; (2) the FT-IR spectra gave no indication of new peaks except those from imide formation; (3) the DSC thermogram of the material cooled and reheated showed only a melting endo-

**Table IV The Curing Temperature Range of the Isomerization for the Model Compound IP-6001 at Different Heating Rates Obtained from the Dynamic DSC and FT-IR Methods**

| Heating Rate | Dynamic DSC            |            |                   | Dynamic FT-IR |                   |                  |
|--------------|------------------------|------------|-------------------|---------------|-------------------|------------------|
|              | Temp. Range            | $T_{\max}$ | $\Delta T_{1/2}$  | Temp. Range   | $T_{\text{flex}}$ | $\Delta T_{1/2}$ |
| 5°C/min      | —                      | —          | —                 | 179–228°C     | 206°C             | 24°C             |
| 10°C/min     | 189–295°C <sup>a</sup> | 245°C      | 67°C <sup>a</sup> | 186–239°C     | 218°C             | 28°C             |
| 15°C/min     | 200–297°C <sup>a</sup> | 253°C      | 60°C <sup>a</sup> | —             | —                 | —                |

<sup>a</sup> The large uncertainty due to peak overlap.



**Figure 3** FT-IR spectra of Thermid IP-600™ at different curing temperatures.

therm; and (4) although “melting” for the imide MC-600™ occurred at 180°C, the aniline terminated version where hydrogen bonding is possible may melt and crystallize at higher temperature; in the case of IP-600™, the crosslinking reaction would suppress the crystallization. The explanation of this second exotherm is not critical for this article because dynamic FT-IR data were only obtained to about 220°C when the isomerization reaction was complete. Table IV presents the dynamic DSC data obtained for this sample using a curve deconvolution procedure.

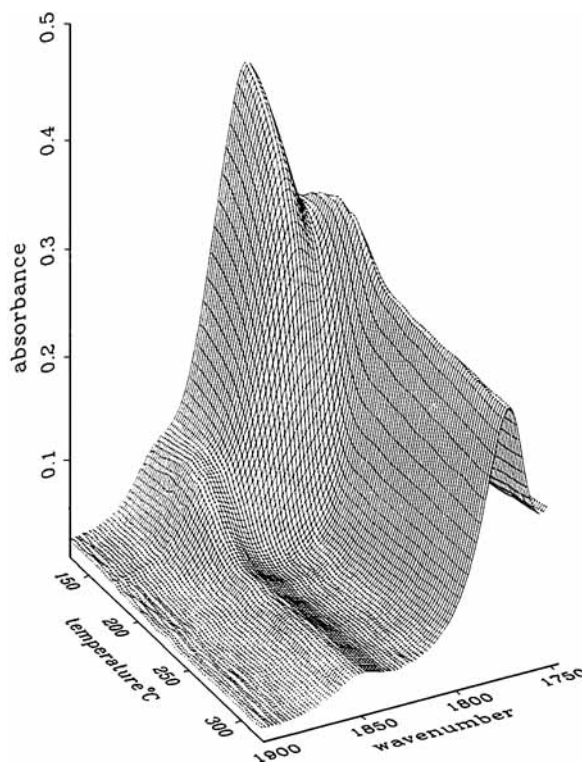
In the dynamic FT-IR experiments, we used information from the DSC thermograms and melting point data to select the 130–320°C temperature range to monitor the isoimide-imide isomerization and crosslinking reactions. To minimize interference from other peaks and to effectively follow these two types of reactions during the thermal curing process, the peak of the isoimidecarbonyl  $\text{>C=O}$  stretching vibration at  $1808\text{ cm}^{-1}$ , which has a strong absorbance intensity, and the peak of the  $\text{C}\equiv\text{CH}-$  stretching vibration at  $3238\text{ cm}^{-1}$ , which has medium absorbance intensity were selected as “windows” to monitor the isoimide-imide isomerization and crosslinking reaction, respectively. FT-IR spectra of Thermid IP-600™ at different curing temperatures are shown in Figure 3. With increasing cure temperature, the isoimide carbonyl group was quickly converted into the imide carbonyl group, while the acetylene terminal group converted more

slowly into the ethylene group. The decrease in absorbance of the isoimidecarbonyl  $\text{>C=O}$  and acetylene  $\text{C}\equiv\text{C}-\text{H}$  vibrations with increasing temperature are shown in Figures 4 and 5, respectively, for the thermal curing process at a heating rate of  $5^\circ\text{C}/\text{min}$ . From these 3-D charts, one can qualitatively observe that there are two different curing temperature ranges for the isoimide-imide isomerization and crosslinking reactions of the polyisoimide Thermid IP-600™, and that these reactions had significantly different kinetics. The isoimide-imide conversion was complete in a shorter time, and thus, at lower temperatures, than the crosslinking reaction, which occurred more gradually and was complete at higher temperatures.

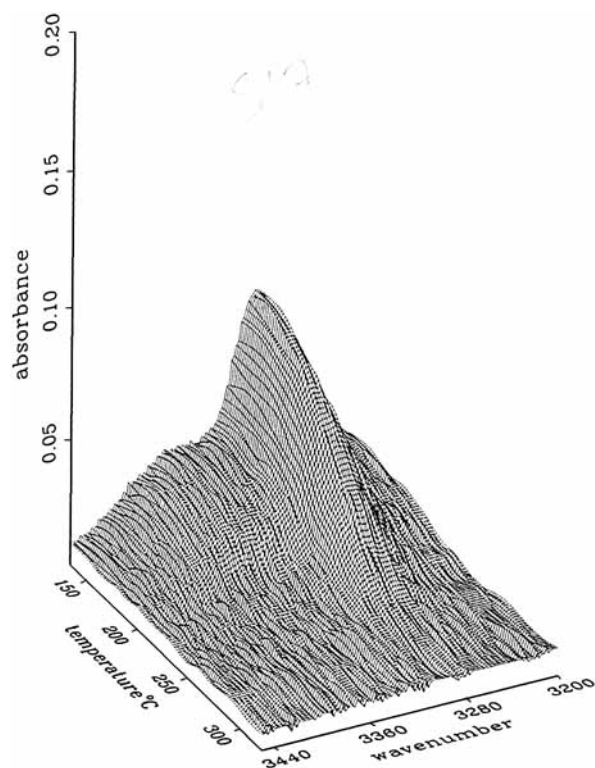
In order to analyze the data quantitatively, we plotted percent conversion of either the isoimide-imide isomerization or crosslinking reaction vs. temperature. A reference peak at  $1478\text{ cm}^{-1}$ , attributed to a benzene ring vibration, which was invariant during the thermal curing process, was used as an internal standard. The percentage conversion was calculated using the following simple equation:

Percent Conversion

$$= [1 - (I_t/I_s)/I_o/I_s] \times 100\%, \quad (1)$$



**Figure 4** Temperature dependence of the isoimide carbonyl group of Thermid IP-600™ during the thermal curing process.



**Figure 5** Temperature dependence of the acetylene group of Thermid IP-600™ during the thermal curing process.

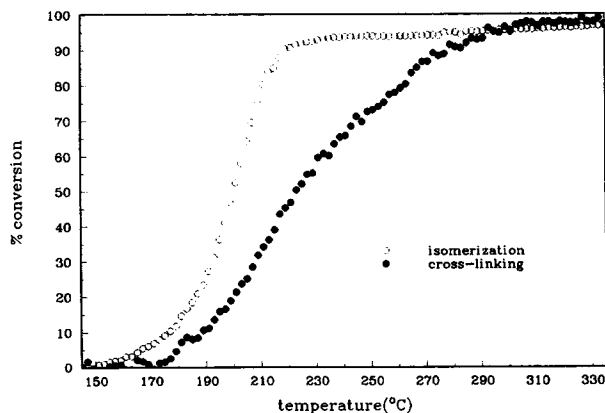
where  $I_t$  and  $I'_s$  represent peak intensities, obtained using integration of the area of the peak after baseline adjustment, of the isoimide carbonyl group or acetylene end groups and internal standard at “ $T$ ” curing temperature, respectively.  $I_o$  and  $I_s$  represent the intensities of the functional groups and the standard at the starting temperature, respectively. Figure 6 presents the profiles of the isoimide-imide isomerization and crosslinking reactions during the thermal curing process at a heating rate of 10°C/min, and shows clearly that the isoimide-imide isomerization and crosslinking reactions occurred over different temperature ranges, although the curing temperature range of the crosslinking reaction spanned most of the isoimide-imide isomerization. The isoimide-imide isomerization started about 15°C below the initiation of the crosslinking reaction and when the isomerization process was complete the crosslinking reaction had reached only half its final value.

Table V lists the results of the dynamic FT-IR data for IP-600™ in terms of the temperature ranges of the reactions, inflection points,  $T_{flex}$  (i.e., the maximum change in % conversion with temperature), and widths,  $\Delta T_{1/2}$  for the isoimide-imide

isomerization and the crosslinking reactions at heating rates of 5°C/min, 10°C/min, and 15°C/min. The widths were obtained by the two points of intersection of three straight lines: (1) the line drawn at low temperature, before significant reaction had occurred (2) the line drawn at high temperature, after the reaction had gone to completion and (3) the line formed at intermediate temperatures tangential to the inflection point. These curves show the same trends as those shown by the DSC curves, i.e., inflection points were shifted to higher temperatures with increasing heating rate, for the same reason discussed previously for  $T_{max}$  from DSC. The dynamic FT-IR data for MC-600™ and the model compound IP-6001 are presented in Table III and Table IV, respectively.

Tables II and V compare the curing temperature ranges of the isomerization and crosslinking reactions of the acetylene-terminated polyisoimide prepolymer by DSC thermal analysis and the dynamic FT-IR method. At the heating rates for which both dynamic DSC and dynamic FT-IR data were obtained, the temperature range for the isomerization and crosslinking reaction of IP-600™ was between 20–30°C larger using dynamic FT-IR than dynamic DSC, indicating that the spectroscopic determination of the isomerization and crosslinking reactions was more sensitive than the calorimetric method. For the same reason,  $\Delta T_{1/2}$  (crosslinking) from the DSC measurements was narrower than  $\Delta T_{1/2}$  (crosslinking) from the FT-IR measurements for MC-600™ (see Table III).

There is good agreement between  $T_{flex}$  (isomerization) and  $\Delta T_{1/2}$  (isomerization) obtained from FT-IR data for IP-600™ and IP-6001 at the same heating rates;  $\Delta T_{1/2}$  for these samples lies between 24–32°C.  $T_{flex}$  (crosslinking) obtained from FT-IR



**Figure 6** Percent conversion of the isomerization and crosslinking reactions of Thermid IP-600™ at a heating rate of 10°C/min.

**Table V** The Curing Temperature Ranges of the Isomerization and Crosslinking Reactions of Thermid IP-600™ at Different Heating Rates Obtained from the Dynamic FT-IR Method

| Heating Rate | Isomerization |            |                  | Crosslinking |            |                  |
|--------------|---------------|------------|------------------|--------------|------------|------------------|
|              | Temp. Range   | $T_{flex}$ | $\Delta T_{1/2}$ | Temp. Range  | $T_{flex}$ | $\Delta T_{1/2}$ |
| 5°C/min      | 160–229°C     | 203°C      | 24°C             | 171–302°C    | 223°C      | 51°C             |
| 10°C/min     | 163–231°C     | 210°C      | 26°C             | 181–329°C    | 237°C      | 60°C             |
| 15°C/min     | 167–235°C     | 213°C      | 32°C             | 186–335°C    | 247°C      | 64°C             |

data from IP-600™ and MC-600™ at the same heating rates is higher by about 20°C for the MC-600™, due its increasing stiffness compared with IP-600™.<sup>14</sup> However, the values of  $\Delta T_{1/2}$  for the crosslinking reaction from the FT-IR data for both samples lie between 49–64°C. Thus, as indicated by qualitative analysis of Figure 6,  $\Delta T_{1/2}$  (crosslinking) is approximately twice  $\Delta T_{1/2}$  (isomerization).

A comparison of  $T_{max}$  and  $T_{flex}$  data for the samples investigated indicated that  $T_{max}$  values from DSC were comparable to the  $T_{flex}$  values from FT-IR. Agreement was particularly good for Thermid MC-600™, for which just a crosslinking reaction occurred. For IP-600™, the value of  $T_{flex}$  (crosslinking) was closer to  $T_{max}$  from DSC.

The dynamic FT-IR method can be used not only for determination of the individual thermal curing temperature ranges of the polyisoimide prepolymer, but also for establishment of kinetic parameters of chemical reactions. The reaction rate for any  $n$ th order chemical reaction can be expressed as

$$\frac{-dC}{dt} = A \left\{ \exp\left(-\frac{E_a}{RT}\right) \right\} C^n, \quad (2)$$

where  $C$  is concentration,  $t$  is time,  $A$  is a preexponential term,  $E_a$  is the activation energy,  $R$  is the gas constant,  $T$  is temperature, and  $n$  is reaction order. In the dynamic FT-IR method, the temperature does not remain constant, but increases as a function of time. The relationship between temperature and time can be expressed  $T = T_o + \varphi t$ , where  $T$  and  $T_o$  are the temperatures at “ $t$ ” and “ $t_o$ ,” respectively,  $\varphi$  is the heating rate, and  $t$  is time. If this equation is differentiated, a derivative ( $dT = \varphi dt$ ) with respect to temperature can be obtained. When  $dT = \varphi dt$  is substituted into eq. (2), it rearranges to give

$$\frac{-dC}{dT} = \frac{AC^n}{\varphi} \left\{ \exp\left(-\frac{E_a}{RT}\right) \right\}. \quad (3)$$

By taking the log of both sides of eq. (2) we can obtain a kinetic equation as a function of temperature, which is similar to the conventional expression using  $t$  as the variable, used for determining kinetic parameters; i.e.,

$$\ln\left(\frac{-dC}{dT}\right) - n \ln C = \ln \frac{A}{\varphi} - \frac{E_a}{RT}. \quad (4)$$

This equation is similar to the equation described by Snyder<sup>15</sup> and Prime<sup>3</sup> who derived the expression for a first-order reaction. In the experiments,  $-dC/dT$  used in eq. (4) can be determined from the slope of the lines between points in a plot of the concentration of functional groups vs. temperature, and  $C$  is the average value between successive concentrations. The value of  $n$  is a constant that depends on the reaction order. These values were then plotted vs. inverse temperature at heating rates of  $\varphi$  5°C/min, 10°C/min, and 15°C/min to obtain  $E_a$  and  $\ln A$ . Based on the dynamic FT-IR data, we used eq. (4) to obtain the kinetic parameters of Thermid IP-600™, MC-600™, and IP-6001. A value of  $n = 1$  was used for the isomerization reaction and a value of  $n = 2$  was used for the crosslinking reaction. Table VI shows the results of the calculation from heating rates of 5°C/min and 10°C/min. Snyder et al. indicated a consistent activation energy can be obtained at heating rates up to 10°C/min in the dynamic FT-IR method.

DSC dynamic data can also be used to calculate the kinetic parameters of the polyisoimide prepolymer. Many articles have been published that use dynamic differential thermal analysis of the chemical reaction kinetics.<sup>16–21</sup> A simple, usable relationship between activation energy  $E_a$ , heating rate  $\varphi$ , and peak exotherm temperature  $T_{max}$  is based on the work of Ozawa:<sup>22</sup>

$$E_a = \frac{-R}{1.052} \cdot \frac{\Delta \ln \varphi}{\Delta(1/T_{max})}, \quad (5)$$



**Table VI Activation Energies of the Isomerization Reaction (First Order) and the Crosslinking Reaction (Second Order) of the Polyisoimide IP0600™, the Model Compound IP-6001, and the Polyimide MC-600™ from Dynamic FT-IR Data**

| Oligomer | $E_a$ (isomerization) |            |         | $E_a$ (Crosslinking) |            |         |
|----------|-----------------------|------------|---------|----------------------|------------|---------|
|          | 5°C/min               | (10°C/min) | Average | 5°C/min              | (10°C/min) | Average |
| IP-600   | 27                    | 26         | 26      | 24                   | 21         | 23      |
| IP-6001  | 33                    | 36         | 34      | —                    | —          | —       |
| MC-600   | —                     | —          | —       | 22                   | 20         | 21      |

\*  $E_a$ -kcal/mol.

which is based on a difference method, where it is not necessary to specify the order of the reaction. The assumption on which the derivation of this equation is based is that the extent of reaction at the peak exotherm is constant and independent of heating rate. The activation energy can be obtained using eq. (5), where  $E_a$  is calculated from data measured at two different heating rates. The average activation energies of Thermid IP-600™, IP-6001, and Thermid MC-600™ obtained in this way using heating rates of 2.5°C/min, 5°C/min, and 10°C/min are given in Table VII. Included also are the values of  $\Delta H$  obtained for the Thermid IP-600™, IP-6001, and MC-600™ samples. As expected,  $\Delta H$  for IP-600™, which includes both the isomerization and crosslinking reaction, is approximately equal to the sum of  $\Delta H$  values from IP-6001 where only the isomerization reaction occurs and MC-600™, where only the crosslinking reaction occurs.

The values of the activation energy obtained from the DSC and FT-IR results are in reasonable agreement. The values from the dynamic FT-IR method are higher for the both the crosslinking and isomerization reactions than the values from the dynamic DSC method. The DSC value for IP-600™ is an activation energy for both the crosslinking and isomerization reactions, and is intermediate between the DSC values obtained for the crosslinking and isomerization reactions from the model compounds. The values of  $E_a$  for MC-600™ agree well with those

reported by Bott.<sup>6</sup> However,  $E_a$  for the IP-600™ determined here calorimetrically is 23.7 kcal/mol (obtained several times) compared with a value of 13.6 kcal/mol obtained calorimetrically by Bott.<sup>6</sup> The similarity in  $E_a$  for all of the reactions may indicate that the rate-limiting step depends on the viscosity. In this case, Arrhenius-type equations used either to analyze DSC or FT-IR data here and previously<sup>6</sup> may not be appropriate.

## CONCLUSION

The dynamic FT-IR method is a new way to determine the individual curing temperature ranges of two or more chemical reactions occurring in one system, if the DSC dynamic method is unable to distinguish these individual temperature ranges for the system of interest. In the dynamic FT-IR method, the two curing temperature ranges of the isomerization and crosslinking reaction of acetylene-terminated polyisoimide prepolymers are clearly separated. The separation makes it possible to obtain kinetic data under isothermal conditions for the individual chemical reactions and to understand the kinetic mechanisms of these reactions.

From the dynamic FT-IR data, we can conclude that: (1) the individual curing temperature ranges of the acetylene-terminated polyisoimide prepolymer, Thermid IP-600™ are approximately 160–

**Table VII Activation Energies of the Polyisoimide IP-600™, the Model Compound IP-6001, and the Polyimide MC-600™ from DSC Data**

| Oligomers                          | IP-600<br>(Crosslinking and Isomerization) | IP-6001<br>(Isomerization) | MC-600<br>(Crosslinking) |
|------------------------------------|--|----------------------------|--------------------------|
| $E_a$ (kcal/mol)                   | 24   | 31                         | 19                       |
| $\Delta H$ (cal/gram) <sup>a</sup> | 58   | 11                         | 37                       |

<sup>a</sup> Average value.

230°C for the isoimide-imide isomerization and 180–330°C for the crosslinking reaction; (2) the reaction rate of the isoimide-imide isomerization is much faster than that of the crosslinking reaction at a particular temperature and occurs at lower temperatures. The individual rate constants of these reactions can be established using FT-IR spectroscopy under isothermal conditions. (3) The isoimide-imide isomerization and crosslinking reactions may affect each other because they occur over the same temperature range during the thermal curing process. For example, during the second half of the crosslinking reaction, the isoimide-imide conversion is complete and, thus, the crosslinking reaction is occurring in the less flexible imide matrix.

The activation energies for the isomerization and crosslinking reactions of IP-600™ have also been determined using the dynamic FT-IR method. The value for the crosslinking reaction was 23 kcal/mol, which compared well with the values of 21 kcal/mol for MC-600™ from dynamic FT-IR and 19 kcal/mol for MC-600™ from dynamic DSC. Values obtained from isothermal measurements<sup>14</sup> were 27.6 kcal/mol for IP-600™ and 24 kcal/mol for MC-600™. The value for the isomerization reaction of IP-600™ was higher, 26 kcal/mol. Dynamic DSC data for IP-600™ gave a composite activation energy for the both the isomerization and crosslinking reactions of 24 kcal/mol, intermediate between the values for the individual reactions. Isothermal measurements<sup>14</sup> obtained for IP-600™ and IP-6001 were 24.7 kcal/mol and 31.7 kcal/mol, respectively.

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