

# Spectroscopic and Thermal Characterization of Poly(glycidyl azide) Converted from Polyepichlorohydrin

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## SYNOPSIS

Poly(glycidyl azide) (PGA) was synthesized by reaction of polyepichlorohydrin (PECH) with sodium azide ( $\text{NaN}_3$ ) by using phase-transfer catalysis. A detailed analysis was performed to follow the polymer-polymer conversion reaction. Conversion of  $-\text{CH}_2-\text{Cl}$  to  $-\text{CH}_2-\text{N}_3$  was achieved completely in 6 h, as determined from FTIR assignment, UV-VIS spectroscopy, and thermal analysis. In FTIR and UV-VIS spectroscopy studies, the reaction was followed from the change in characteristic peak intensities. Thermal analysis also showed that the first thermal decomposition process of PGA, which is due to the exothermic cleavage of pendant  $-\text{N}_3$  groups, was shifted to higher temperatures, and the exothermicity was increased as the conversion proceeded. It was also found that the extent and completion of  $-\text{Cl}$  to  $-\text{N}_3$  conversion could be easily followed by measuring the glass transition temperature and exothermic decomposition of the polymers. The quantitative analysis of the data collected from FTIR and DSC measurements showed that  $\text{PECH} \rightarrow \text{PGA}$  conversion is a first-order reaction with a rate constant of  $k = 0.74 \text{ h}^{-1}$ . © 1996 John Wiley & Sons, Inc.

## INTRODUCTION

In the preparation of typical composite solid propellants, a functionally active liquid prepolymer is mixed with solid particulate oxidizer, metallic fuel, plasticizer, and other minor ingredients. Upon addition of crosslinking agent for the liquid prepolymer, the well mixed and uncured viscous propellant slurry can be transferred into a previously prepared rocked motor casing having a desired geometrical configuration. The filled motor casing is then heated to curing temperature (preferably 60–70°C) and held at that temperature until the urethane reaction is complete and the viscous and uncured slurry is converted to a solid, elastomeric, and polyurethane matrix.

In the composite propellant technology, the most commonly used prepolymers are low molecular weight ( $M_n \cong 2000\text{--}3000$ ) liquid polybutadienes or their copolymers having epoxy, carboxy, or hydroxy functional groups. For carboxy-terminated prepolymers, aziridinyl or epoxy curing agents could be used. If the prepolymer possesses hydroxy functional groups, isocyanate functional curing agents could be used for the propellant system.

During the last decade, materials having highly energetic  $-\text{N}_3$  groups such as 3,3-bis(azido-methyl)oxetane polymer, azido oxetan monomer, 3-azidomethyl 3-methyl oxetane, and poly(glycidyl azide) (PGA) were developed for use in the preparation of crosslinked or uncrosslinked composites for double base propellants.<sup>1–6</sup>

PGA, a typical example of these azido materials, is a low molecular weight ( $M_n \cong 2000$ ), difunctional hydroxyl-terminated liquid prepolymer having a polyether main chain structure and relatively low glass transition temperature ( $T_g = -48^\circ\text{C}$ ), low viscosity ( $2.4 \times 10^3 \text{ cps}$  at  $25^\circ\text{C}$ ), and relatively high density as compared to other propellant binders.<sup>7</sup>

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The terminal —OH groups of PGA can be cured with —NCO groups of isocyanates and crosslinked with low molecular weight and polyfunctional hydroxyl compounds. These are necessary for good propellant processing and desirable physical properties. PGA has positive heat of formation (+957 kJ/kg).<sup>8</sup> This provides easy and rapid decomposition of this polymer at relatively low temperatures. Therefore, these unique properties of PGA attracted the interest of scientists working on propellant technology, and a number of studies have focused on the synthesis and application of PGA.<sup>3-7,9-12</sup>

PGA has pendant azidomethyl groups that impart additional performance benefit to PGA-based propellants. Because of their unique thermal decomposition properties, the combustion and thermal decomposition of PGA and some other azide polymers were investigated in detail.<sup>1,2,8</sup> Kubota and Sonobe<sup>8</sup> showed that the thermal decomposition mechanism of PGA consists of two weight-loss steps. The first main weight-loss step reflects the exothermic cleavage of pendant azide groups resulting in a polyacrylonitrilelike structure. The second main weight-loss step corresponds to degradation of the remaining polyether main chain.

The object of this study was to follow the conversion of polyepichlorohydrin (PECH) into PGA by using spectroscopic and thermal analysis methods. In FTIR and UV-VIS spectroscopy studies, the extent of the conversion was ascertained from the change in characteristic peak intensities. Thermal analysis studies were also performed to follow changes in the thermal behavior of the reaction product as conversion proceeded.

## EXPERIMENTAL

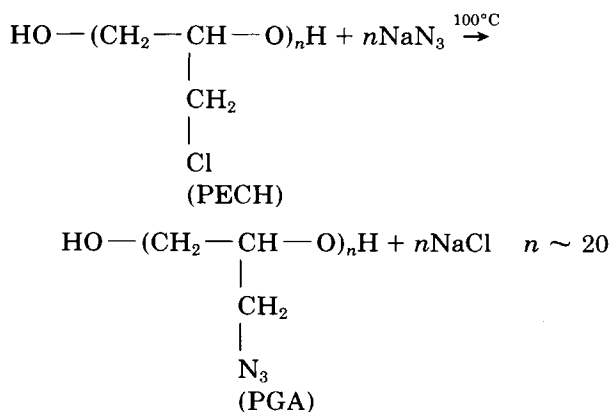
### Materials

(PECH) was obtained from 3M (U.S.A.) under the trade name of HX-102 and was used without further purification. Its molecular weight was found to be 1810 g/mol and its hydroxyl value was 1.14 meq/g.<sup>7</sup> Sodium azide (NaN<sub>3</sub>) was purchased from Merck at better than 98% purity. PGA was synthesized by the reaction of PECH with NaN<sub>3</sub> following the procedure described in the literature.<sup>4,7</sup> It has a number average molecular weight of 2200 g/mol as determined by vapor phase osmometry. The hydroxyl equivalent was determined as 0.94 meq/g according to the method cited in Dee et al.<sup>13</sup> The composition of the polymer as determined from elemental anal-

**Table I** Elemental Analysis Results of PGA (Wt %)

	C	N	H
Theoretically calculated	36.36	42.42	5.05
Experimentally determined	35.95	42.23	5.11

ysis is shown in Table I. The chemical equation for this conversion reaction is designated as follows:



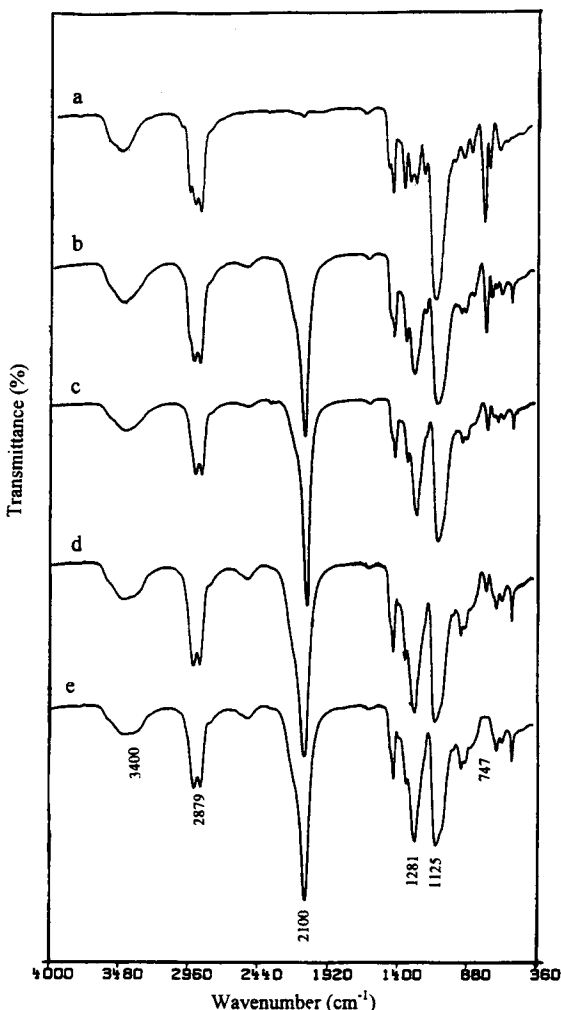
### Instrumentation

Thermal analysis of polymer samples was conducted using a DuPont TA 9900 Thermal Analyzer System equipped with model 951 thermogravimetry and model 910 differential scanning calorimetry (DSC) systems. All analyses were conducted in dynamic N<sub>2</sub> atmosphere at 25 mL/min at a 10°C/min heating rate. FTIR spectra were collected on a Nicolet 520 spectrometer with KBr cell. The elemental analysis results of PGA were obtained by using a Carlo Erba Elemental Analyzer (model 1106).  $\bar{M}_n$  values of PECH and PGA were determined by using a Knauer Vapor Phase Osmometer.

UV-VIS spectra were taken of polymer solutions at a concentration of 1 mg/mL in THF on a Philips model PU-8715 spectrophotometer. GPC chromatograms were taken by using a Waters 510 HPLC pump with a Waters 410 differential refractometer and a Waters styragel HT6E + HR1 column system. THF was the elution solvent with a 1 mL/min flow rate at 40°C.

## RESULTS AND DISCUSSION

For the spectroscopic characterization of converting PECH into PGA, a baseline FTIR spectrum of



**Figure 1** FTIR spectra of PECH and the samples taken from the reaction medium at different time intervals. (a) PECH, (b) 0.5 h, (c) 1.0 h, (d) 2.0 h, and (e) 6.0 h.

PECH was recorded. In the IR spectrum of PECH given in Figure 1(a), the strong peak observed at  $1125\text{ cm}^{-1}$  is due to the C—O—C ether bridge of the polyether main chain whereas the sharp peak at  $747\text{ cm}^{-1}$  is the vibrational band of  $\text{CH}_2\text{—Cl}$  bonds.

In FTIR spectra of PGA, the sharp absorbance peaks at  $2100$  and  $1281\text{ cm}^{-1}$  are due to  $\text{CH}_2\text{—N}_3$  bonds. To follow the extent of reaction conversion from PECH to PGA, any of these characteristic peaks can be used. The disappearance of the  $\text{CH}_2\text{—Cl}$  band or appearance of the two  $\text{CH}_2\text{—N}_3$  bands with time can be monitored to check and control the reaction completion. Moreover, the sharp absorbance peak of the C—O—C ether bridge of PECH can be clearly seen at  $1125\text{ cm}^{-1}$ . One-half hour after the beginning of the reaction, the exis-

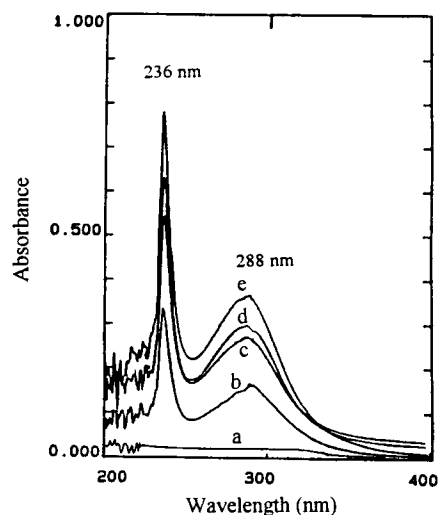
tence of sharp peaks at  $2100$  and  $1281\text{ cm}^{-1}$  confirm the formation of  $\text{CH}_2\text{—N}_3$  bonds, even at the early stage of the reaction.

During the course of the reaction conversion, the intensity of the characteristic band of  $\text{CH}_2\text{—Cl}$  at  $747\text{ cm}^{-1}$  decreases as the intensity of  $\text{CH}_2\text{—N}_3$  band at  $2100$  and  $1281\text{ cm}^{-1}$  increases [Fig. 1(b–e)]. After 6 h, the peak at  $747\text{ cm}^{-1}$  corresponding to  $\text{CH}_2\text{—Cl}$  bonds disappeared, indicating that the reaction is complete in 6 h.

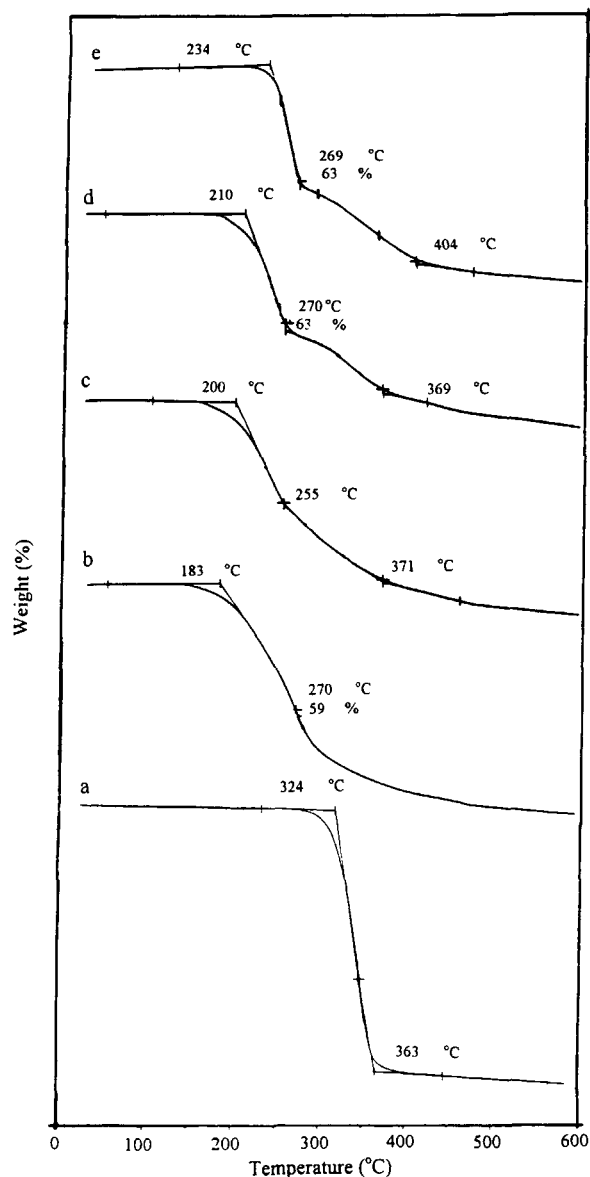
The hydroxyl groups at  $3400\text{ cm}^{-1}$  originally present at the chain ends of PECH are retained during and after completion of the conversion of PECH into GPA. This is an extremely important feature for further crosslinking of PGA into solid propellant matrix.

Although it is evident from the FTIR spectra of PECH and PGA that the structures yielding absorbances at  $1125$  and  $3400\text{ cm}^{-1}$ , which are due to ether linkages on the main chain and hydroxyl group at the chain ends, respectively, are retained during the course of the conversion. This was also checked with a GPC analysis. The chromatograms recorded for PECH and PGA obtained therefrom were exactly identical.

The course of the  $\text{PECH} \rightarrow \text{PGA}$  reaction was also followed by recording UV-VIS spectra of different samples after 0.5, 2, 4, and 6 h from the initiation of the reaction [as given in Fig. 2(b–e)]. PECH is nonabsorbant in the UV-VIS region [Fig. 2(a)]. The two strong absorbance peaks at  $236$



**Figure 2** UV-VIS spectra of PECH and different samples taken from the reaction medium at different time intervals. (a) PECH, (b) 0.5 h, (c) 1.0 h, (d) 2.0 h, and (e) 6.0 h.

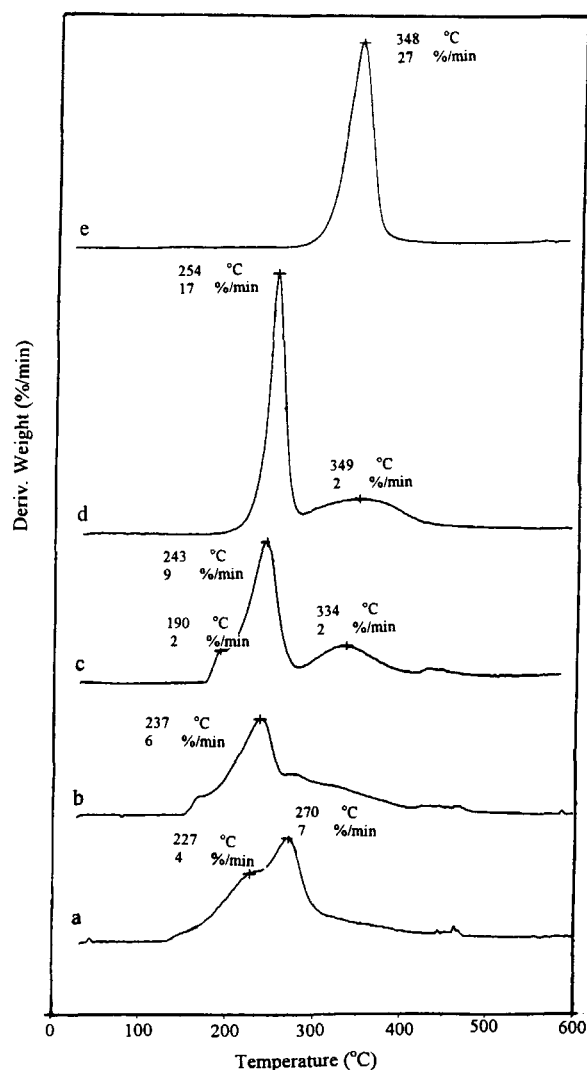


**Figure 3** TGA curves of PECH and the samples taken from the reaction medium at different time intervals. (a) PECH, (b) 0.5 h, (c) 1.0 h, (d) 2.0 h, and (e) 6.0 h.

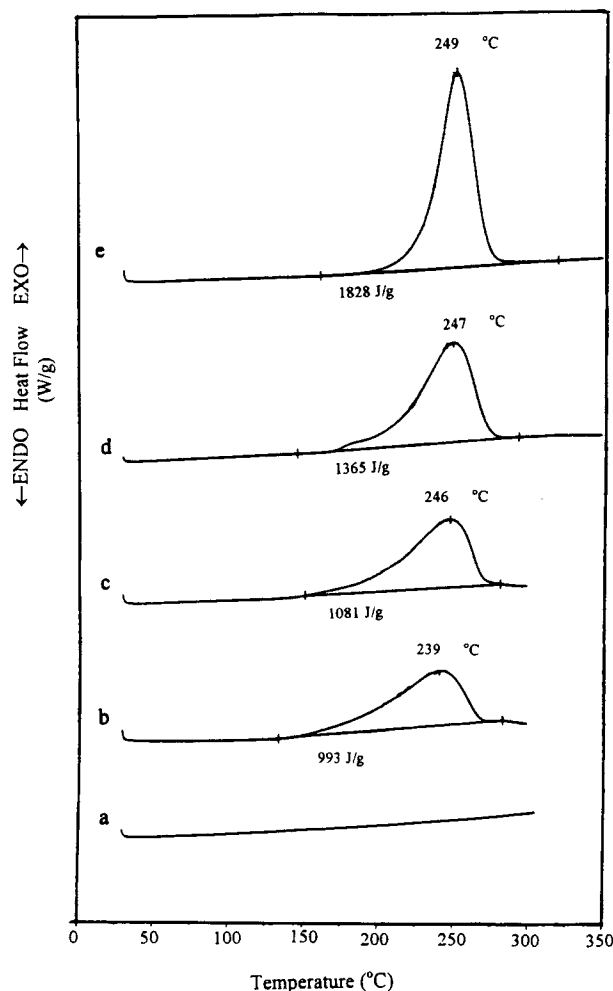
and 288 nm are probably due to two different resonances of nitrogen bonds in the  $-\text{N}_3$  group (i.e.,  $-\text{CH}_2-\text{N}^--\text{N}=\text{N}^+$  and  $-\text{CH}_2-\text{N}^--\text{N}^+\equiv\text{N}$ ). The absorption intensities at these two wavelengths 0.5 hour after the start of the reaction [Fig. 2(b)] are very strong, supporting the idea that the conversion of  $-\text{Cl}$  groups to  $-\text{N}_3$  groups is highly efficient even at the early stage of the reaction.

In addition to IR and UV-VIS spectroscopies used to follow the substitution of  $-\text{Cl}$  groups by  $-\text{N}_3$

groups, thermal analysis techniques were also employed to characterize the intermediate and final products of conversion. In Figure 3, dynamic thermogravimetric traces are given for PECH and polymer samples taken from the reaction medium at different time intervals (as explained in the figure caption). The lowermost curve is the thermogram of PECH and the uppermost curve is that of PGA. While PECH degrades in a single step [Fig. 3(a)], the degradation of PGA takes place in two steps. As the conversion of PECH into PGA proceeds, the thermogram takes the shape of the PGA curve. The comparison of weight-loss curves of polymers with different extents of conversion can be better made by referring to the derivative weight-loss curves of



**Figure 4** DTG curves of thermograms shown in Figure 3. (a) 0.5 h, (b) 1.0 h, (c) 2.0 h, (d) 6.0 h, and (e) PECH.



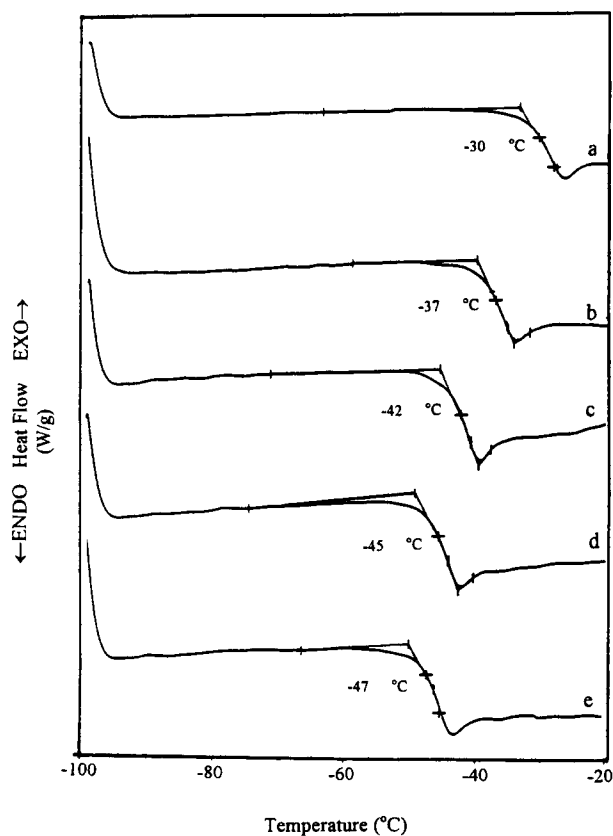
**Figure 5** DSC curves of PECH and samples taken from the reaction medium at different time intervals. (a) PECH, (b) 0.5 h, (c) 1.0 h, (d) 2.0 h, and (e) 6.0 h.

the thermograms displayed in Figure 3 (see Fig. 4). The extent and the success of converting  $-\text{Cl}$  into  $-\text{N}_3$  groups are more evident in this figure. The derivative curve of the sample in the form of a broad peak with a shoulder at around  $227^\circ\text{C}$  gradually changes into two characteristic decomposition peaks of PGA.<sup>14</sup> The sharp low temperature peak ( $255^\circ\text{C}$ ) corresponds to removing pendant  $-\text{N}_3$  groups from the main chain, and the broad peak with a maximum at  $350^\circ\text{C}$  results from degradation of the main chain that nearly corresponds to the maximum weight-loss temperature of PECH degradation. The area of the peak corresponding to  $-\text{N}_3$  elimination continuously increases as the extent of the conversion increases.

DSC was also used as a thermal analysis method for the characterization of initial, final, and inter-

mediate products of the  $\text{PECH} \rightarrow \text{PGA}$  conversion reaction. The loss of  $-\text{N}_3$  groups as observed in Figures 3 and 4 is a strongly exothermic process that is easily identified by DSC. In Figure 5, the DSC thermograms of PECH and PGA are given together with those of partially converted PECH in the temperature interval  $150\text{--}300^\circ\text{C}$ . It was shown in our recent publication that the overall exothermicity of first-stage decomposition is solely due to  $-\text{N}_3$  elimination.<sup>14</sup> The peak area corresponding to this exothermic reaction is directly related to the amount of  $-\text{N}_3$  groups present in the main chain. Figure 5 clearly shows that the area under this peak increases with an increasing extent of conversion. At the end of 6 h, the conversion is complete and the exothermicity reaches that of pure PGA, for example,  $\approx 1828 \text{ J/g}$ .

Furthermore, to characterize the converted products by DSC, we measured the glass transition temperatures of samples taken from the reaction medium over different intervals of time. The glass transition temperature of pure PECH is found to be



**Figure 6**  $T_g$  curves of PECH and the samples taken from the reaction medium at different time intervals. (a) PECH, (b) 0.5 h, (c) 1.0 h, (d) 2.0 h, and (e) 6.0 h.

**Table II** Quantitative Analysis of FTIR and DSC Data

Time (h)	Intensity of C—H Peak at 2873 cm <sup>-1</sup> (mm) (A)	Intensity of C—Cl Peak at 747 cm <sup>-1</sup> (mm) (B)	C = (B)/(A)	X <sub>(FTIR)</sub>	X <sub>(DSC)</sub>
0.0	21.74	21.82	1.004 = Co	0.00	0.00
0.5	22.56	13.90	0.616	0.38	0.54
1.0	—	—	—	—	0.59
1.5	20.35	7.15	0.351	0.65	—
2.0	21.60	4.03	0.187	0.81	0.74
3.0	16.66	1.20	0.072	0.92	0.82
4.0	17.81	0.83	0.047	0.95	0.95
5.0	23.00	0.65	0.028	0.97	0.99
6.0	17.20	0.00	0.000	1.00	1.00

−30°C, whereas that of PGA is −48°C. This difference is obviously due to replacement of —Cl groups by —N<sub>3</sub> groups. It would therefore be possible to follow the extent of conversion by carefully determining the glass transition temperature of partially converted samples. Figure 6 shows the thermograms (with  $T_g$  values) determined for pure PECH, PGA, and those of intermediate products. These traces clearly demonstrate that as the concentration of —N<sub>3</sub> groups incorporated into the main chain of PECH is increased, the  $T_g$  decreases, finally reaching that of pure PGA.

The qualitative investigation of PECH → PGA conversion as substantiated by various methods was also treated quantitatively. For this purpose the data collected by FTIR and DSC techniques were utilized. Table II shows the intensities of two characteristic bands appearing at 747 and 2873 cm<sup>-1</sup> corresponding to diminishing CH<sub>2</sub>—Cl and unchanging C—H

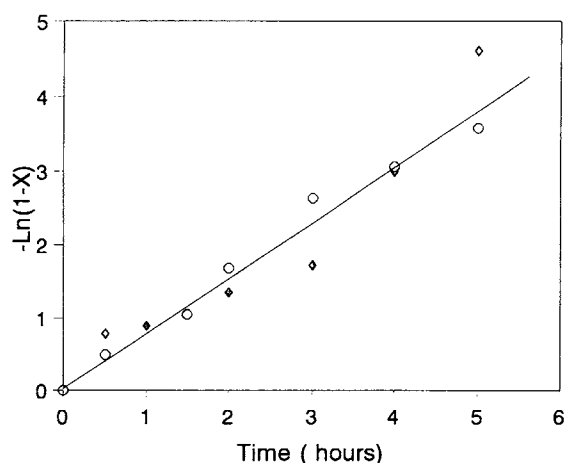
absorbances. By taking the ratio of absorbances at 747 versus 2873 cm<sup>-1</sup>, one can quantify the extent of conversion. These ratio values and corresponding conversions are also listed in Table II. The plot of conversion against time, assuming a first-order reaction, yielded a linear relation as shown in Figure 7 with a rate constant of  $k = 0.74 \text{ h}^{-1}$ . The extent of conversion is also determined from the exothermic peak areas of DSC traces given in Figure 5. The fractional conversion has been determined from the ratio of  $\Delta H_t / \Delta H_\infty$  where  $\Delta H_t$  and  $\Delta H_\infty$  refer to heat of decomposition of —N<sub>3</sub> groups at time  $t$  and infinity. The relevant data is also collected in Table II and a corresponding plot is shown in Figure 7. The agreement between the two curves is very good.

In conclusion, this detailed experimental work utilizing FTIR and UV-VIS spectroscopic techniques, as well as thermogravimetric analysis, DTG, and DSC, has shown that the polymer-polymer conversion reaction between PECH and PGA can be easily and reliably followed both qualitatively and quantitatively.

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**Figure 7** Plots of the conversion data obtained from FTIR and DSC as a function of time. (●) FTIR and (◆) DSC.

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