Thermal Decomposition of Poly(glycidyl azide) as Studied by High-Temperature FTIR and Thermogravimetry

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SYNOPSIS

Thermal decomposition of poly(glycidyl azide) (PGA) has been studied by using thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), and high-temperature FTIR spectrometry. By using DSC and TGA techniques, the first stage weight loss of PGA due to exothermic decomposition of pendant azide ($-N_3$) groups was explained in terms of the energy released at every stage of decomposition. From the glass transition temperature (T_g) measurements, it was observed that T_g values of PGA increased with increasing quantity of decomposed $-N_3$ groups. The course of the decomposition reaction was also studied by taking successive FTIR spectra. It was observed that during the first stage weight loss process of PGA, the main chain was not decomposed thermally; inter- and intramolecular linking reactions accompanied the side chain decompositions. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Solid propellants are prepared from a mixture of an oxidizer, fuel, and other additives together with a suitable polymeric binder to impart mechanical integrity. Recently polymers having pendant azidomethyl groups were developed as highly energetic propellant binders, plasticizers, and gas generators. Poly(glycidyl azide) (PGA) is a typical example of these energetic polymers that decompose very rapidly even at low decomposition temperatures and produce fuel-rich decomposition products.[1] Though the azide polymers contain relatively small amounts of oxygen, the heat released is considered to be due to the scission of the $-N_3$ bond structure to form N_2. PGA can be synthesized by the reaction of polyepichlorohydrin (PECH) with sodium azide (NaN_3).[2-6] PGA has high energy potential and relatively low detonation sensitivity properties. These unique properties of PGA make it possible to use it in the preparation of highly energetic, high specific im-

pulse, high burning rate, and smokeless propellants. In propellant compositions a great degree of safety handling and reduced sensitivity to detonation are desired. PGA has also become a superior replacement for nitroglycerine in either crosslinked and uncrosslinked composite-modified double base propellants, which yield improved safety advantages.[7] These unique properties of PGA therefore have attracted the interest of scientists working in closely related fields[8-10] and great effort has been performed for the application of PGA on modern rocket propellants.

The objective of this work is to study the thermal decomposition behavior of PGA by DSC and TGA and to explain the changes in the chemical structure of this polymer at elevated temperatures in the course of the decomposition reaction by using FTIR spectroscopy with high temperature accessories.
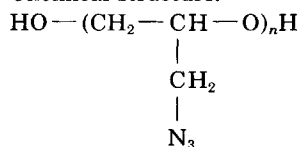
EXPERIMENTAL

Materials

The PGA used in this study was synthesized by the reaction of PECH with NaN_3 at 100°C.[4,6] The product was a yellowish viscous liquid. The chemical structure and thermochemical properties of synthesized PGA are listed in Table I.

Table I Some Properties of PGA

Chemical structure:

HO—(CH$_2$—CH—O)$_n$H
        |
       CH$_2$
        |
       N$_3$

Number average molecular weight ($\bar{M}_n$): 2200 g/mol
OH equivalent: 0.93 equiv/g
Density: 1.29 g/cm^3
Viscosity: 2.4 × 10^3 cps
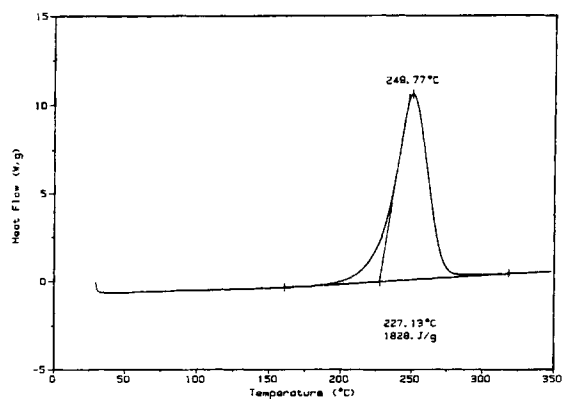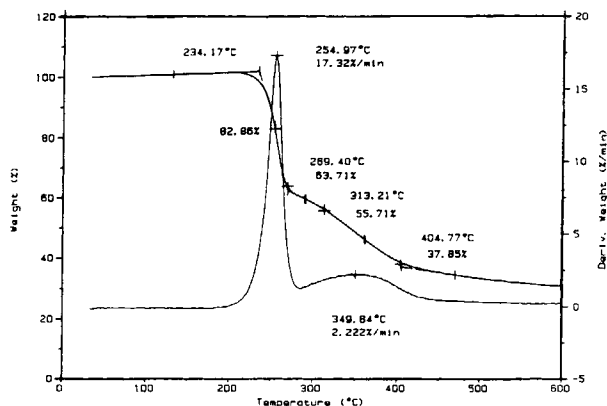
Elemental analysis results:

|	C	H	N	O
Theoretical (%)	36.36	5.05	42.42	16.17
Experimental (%)	35.95	5.11	42.23	17.36

PECH was obtained from 3M Company under the trade name of HX-102 and sodium azide was supplied by Merck; these were used without further purification.

Instrumentation

DSC and TGA measurements were carried out by using Du Pont DSC-9100 and TGA-951, respectively, with a TA-9900 data processing system, under nitrogen atmosphere and at heating rate of 10°C/ min. The DSC was calibrated with metallic indium (99.99% purity) and the TGA was calibrated with calcium oxalate. T_g values were determined at half-height of the displacement.

For spectroscopic measurements a Nicolet 520 FTIR spectrometer together with Specac model temperature controlling system with high temperature cell were used. The PGA loaded high-temper-

Figure 2 TGA thermogram of PGA.

Figure 1 DSC thermogram of PGA.
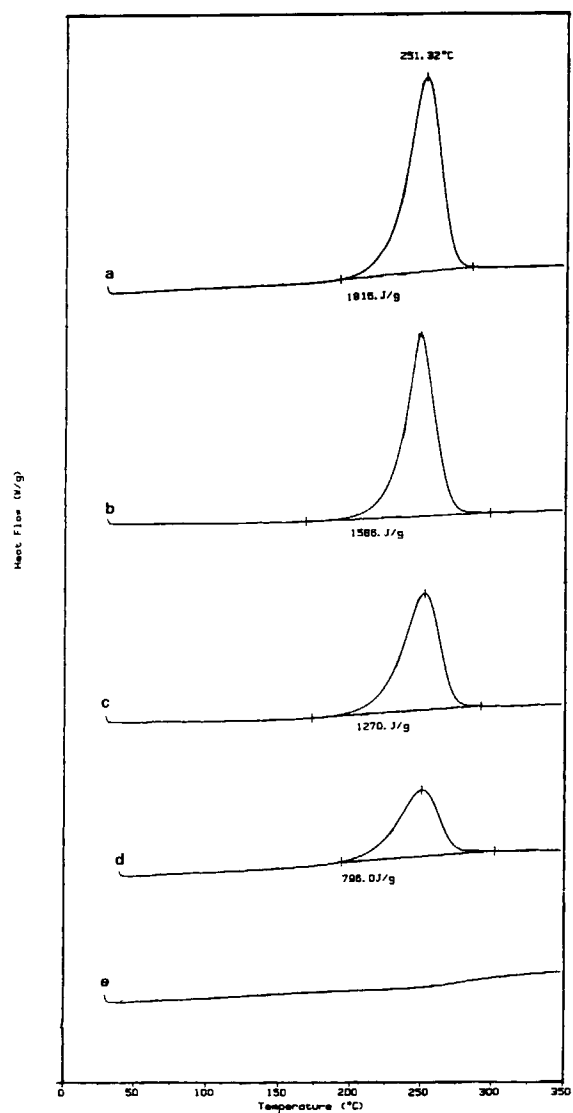
Figure 3 DSC curves of PGA samples preheated to the following temperatures: (a) 213°C, (b) 225°C, (c) 237°C, (d) 245°C, and (e) 270°C.
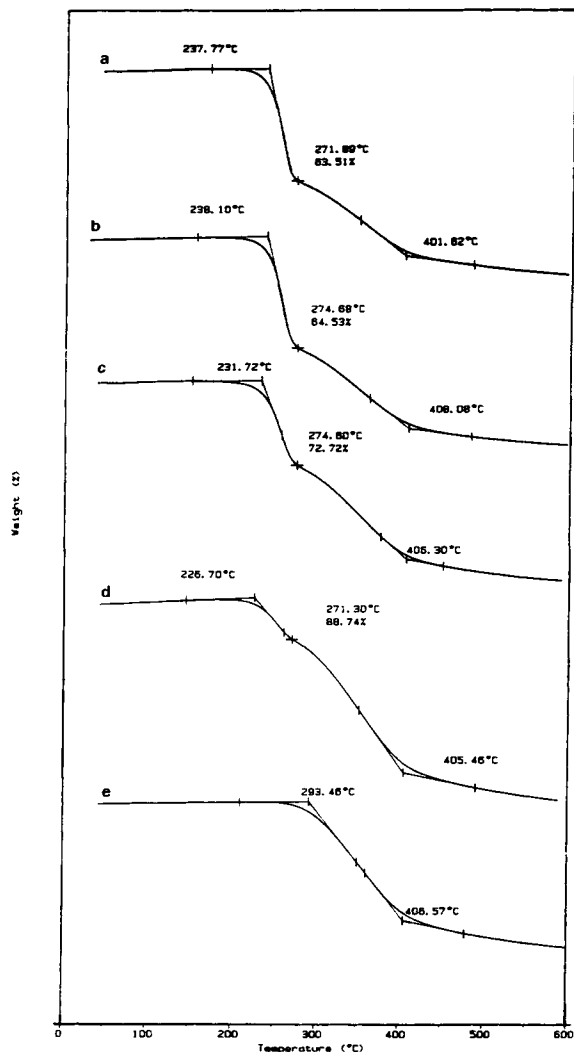
Figure 4   TGA curves of PGA samples preheated to the following temperatures: (a) 213°C, (b) 225°C, (c) 237°C, (d) 245°C, and (e) 270°C.

ature cell was gradually heated up to 210°C, which is the onset temperature of —N_3 groups decomposition. The heating rate was 1°C/min and temperature was kept constant for half an hour after every 10°C elevation of cell temperature. In the course of the heating process, successive IR spectra of the sample were taken and all structural changes were followed on a real time basis.

RESULTS AND DISCUSSION

Thermal decomposition of polymeric binder plays an important role in the combustion of solid propellants. For this reason it is necessary and important to understand the thermal degradation process

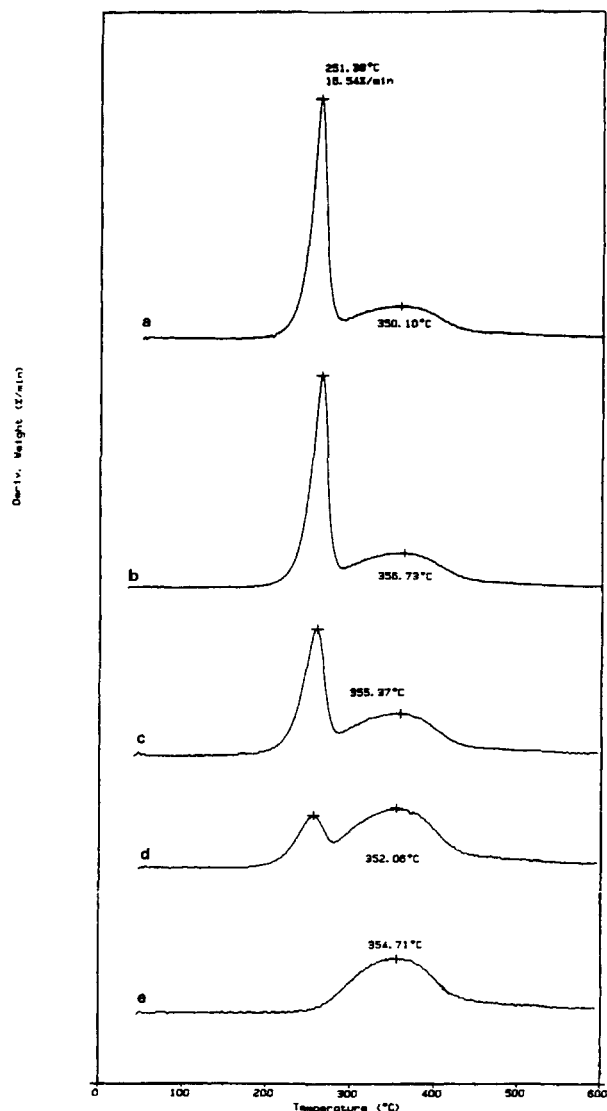of PGA. To understand the thermal decomposition mechanism, first TG and DSC curves of PGA were recorded.

Figure 1 shows the DSC thermogram of PGA. The single exothermic peak observed at around 250°C is due to the elimination of N_2 from the azide group forming the first stage of the decomposition process. The energy liberated at this stage is 1828 J/g. In weight loss and derivative of weight loss curves of PGA (Fig. 2) two characteristic weight loss steps are observed. The first decomposition is the major process and corresponds to nearly 36% weight loss, which starts at 210°C and ends around 270°C. The second stage is completed nearly at 410°C. These two weight loss stages are clearly depicted in the derivative thermograms.

The elimination of N_2 from the repeating unit of PGA stoichiometrically corresponds to a 30% weight loss. The percentage weight loss reached at the end of first derivative peak is, however, 36%. The temperature interval of first peak in the derivative thermogram exactly coincides with the exothermic peak of DSC curve. The first step in the TGA trace is, therefore, designated as side chain decomposition. A slight overlap between the end of this process with the main chain degradation causes the weight loss observed to be 36% rather than 30%.

To understand the two stage decomposition processes of PGA, thermally degraded PGA samples were prepared by preheating the pure polymer up to different temperatures between 213°C (onset of decomposition) and 270°C (almost the end of decomposition). After every preheating process, thermally partially degraded samples were cooled down to room temperature, and their TGA and DSC traces were again recorded.
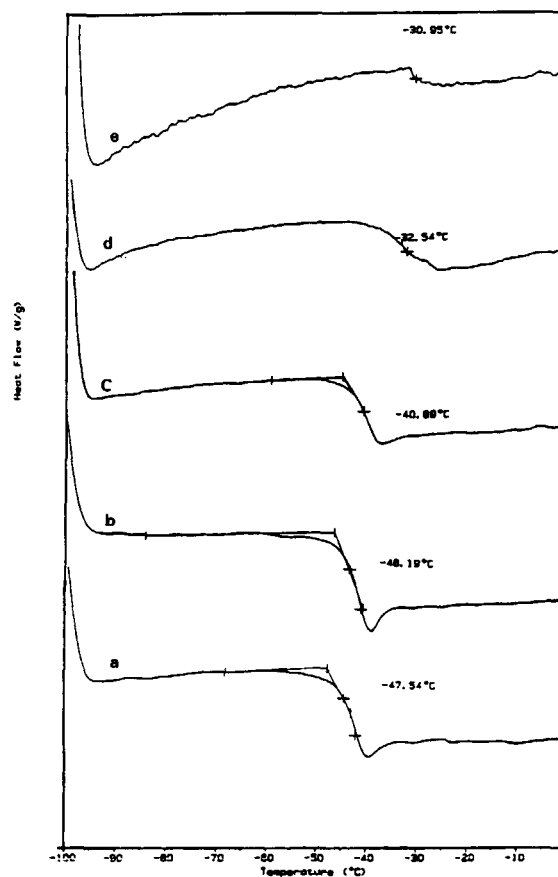
From the DSC curves of thermally degraded PGA samples in Figure 3, it is observed that the areas of exothermic peaks that are due to the decomposition of —N_3 groups decrease as the preheating temperature increases. Finally for the sample preheated to 270°C no exothermic peak has been observed. This result can be taken as proof of the decomposition reaction of pendant —N_3 groups that is completed at 270°C. This result is also supported by TG and DTG curves given in Figures 4 and 5, respectively, and they are consistent with preliminary findings[1,10] where 3-azidomethyl 3-methyl oxetane (AMMO) was used as another azide type polymer.

From the dynamic TGA curves of thermally degraded PGA samples in Figure 4, it can be seen that as the preheating temperature is increased, the first stage weight loss due to the quantitative decomposition of —N_3 groups decrease. Finally, as shown
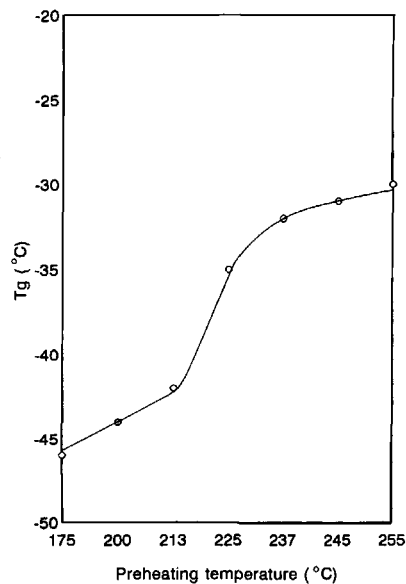
Figure 5 DTG curves of thermograms of Figure 4. (a) 213°C, (b) 225°C, (c) 237°C, (d) 245°C, and (e) 270°C.

Figure 6 Glass transition temperatures of original and thermally degraded PGA samples: (a) original PGA, (b) 175°C, (c) 213°C, (d) 225°C, and (e) 255°C.

from the TGA curves of the PGA sample, which is preheated up to 270°C (Fig. 4), the first stage weight loss was eliminated completely and only the second stage weight loss process was observed. This indicates that in the course of the thermal decomposition process of PGA, all $-N_3$ groups were totally eliminated at 270°C, as has already been proved by DSC work. The derivatives of the curves given in Figure 4 are collectively shown in Figure 5. It is well known that areas under the peaks in a derivative thermogram are direct quantitative measures of the reactions corresponding to those specific peaks. The first sharp peak due to azide group decomposition showed a steady decrease as the preheating temperature was increased. It is completely lost for the sample heated to 270°C (lowermost curve in Fig. 5). The second

**Figure 7** Plot of T_g value of PGA samples as a function of preheating temperature.
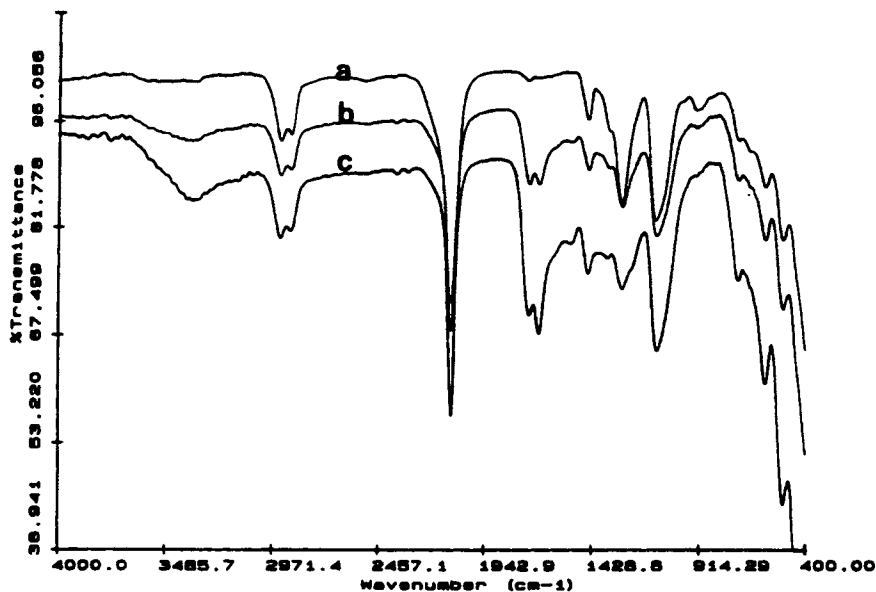
Figure 8   FTIR spectra of PGA recorded at different temperatures (4000–400 cm⁻¹): (a) 170°C, (b) 200°C, and (c) 210°C.

broad peak, which corresponds to second stage decomposition reactions, retained its shape and character during these preheating processes.
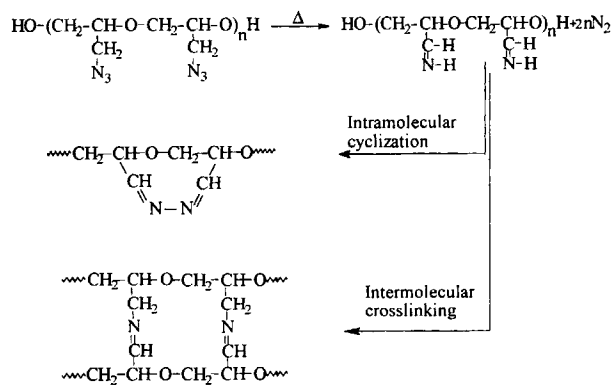
A low T_g value is usually considered as an indication of superior physicochemical properties for a propellant binder. PGA has a lower T_g value (−48°C) compared to its precursor polymer, PECH (−30°C). It is clear that this significant difference between T_g values of PGA and PECH is due to the substitution of —N₃ groups for —Cl. As has al-

ready been shown by the preheating procedure, the azide groups can be removed in a controlled way; it would therefore be interesting to determine the T_g values of these partially degraded samples.

In Figure 6, DSC traces of original PGA and those of thermally degraded samples are shown. As is clear from Figure 6, the elimination of —N₃ groups from the main chain caused a continuous increase in the T_g values of thermally degraded samples. This phenomenon can be clearly seen when T_g values of pre-
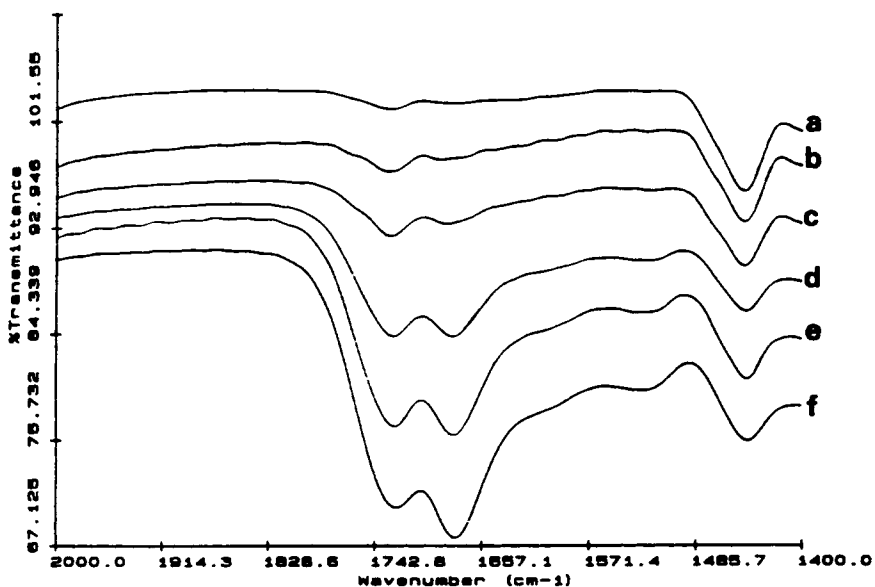
Figure 9   FTIR spectra of PGA recorded at various temperatures (2000–1400 cm⁻¹): (a) 170°C, (b) 180°C, (c) 190°C, (d) 200°C, (e) 208°C, and (f) 210°C.

HO-(CH$_2$-CH-O-CH$_2$-CH-O)$_n$H $\xrightarrow{\Delta}$ HO-(CH$_2$-CH-O-CH$_2$-CH-O)$_n$H+2nN$_2$
  |CH$_2$ |CH$_2$ |C-H |C-H
  |N$_3$ |N$_3$ |N-H |N-H

                                              Intramolecular
                                              cyclization

~~~CH$_2$-CH-O-CH$_2$-CH-O~~~
       \CH   CH/
        \N—N/

~~~CH$_2$-CH-O-CH$_2$-CH-O~~~   Intermolecular
       |CH$_2$ |CH$_2$ crosslinking
       |N |N
       |CH |CH
~~~CH$_2$-CH-O-CH$_2$-CH-O~~~

Scheme 1

heated samples are plotted as a function of pre-heating temperature in Figure 7. As the preheating temperature was increased, a sudden increase in T_g values of thermally degraded samples was observed at around 213°C. Further increase in the T_g values of partially degraded PGA chains is due to crosslinking processes taking place intermolecularly. This has been confirmed by the insolubilities of these samples and their swelling in otherwise soluble liquids.

The —N$_3$ groups elimination from the main chain of polymer was also followed by taking real time IR spectra of PGA sample gradually heated up to 210°C. These spectra are shown in Figures 8 and 9. A decrease in the intensity of —N$_3$ groups at 2100 and 1280 cm^{-1} was observed at 170°C and the new peaks appeared at 1529, 1677, 1725, and 3350 cm^{-1} due to N—H bending, —C=N—C—H, —C=N—C—C, and N—H stretching, respectively. As the cell temperature was increased, an increase in the intensity of these peaks was observed. An increase in the intensity of the peaks at 1677 and 1724 cm^{-1} can be clearly observed in Figure 9. It is interesting to note that the intensities of the peak at 1410 cm^{-1}, which is due to C—O—C ether

bridge of the PGA main chain, remained unchanged during the initial stage of decomposition reaction. This indicates that in the course of the first decomposition process, the PGA main chain was not affected by thermal degradation.

The spectroscopic determination of —C=N—C— type structures and insolubility of partially degraded samples implied the formation of inter- as well as intramolecular bridges among the PGA chains. Taking these findings into consideration, we propose the reactions shown in Scheme 1 as possible routes to these formations.

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