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### Synthesis and Characterization of Glycidyl Azide Polymer with Enhanced Azide Content

Y. Murali Mohan<sup>a</sup>; K. Mohana Raju<sup>a</sup>; B. Sreedhar<sup>b</sup>

<sup>a</sup> Synthetic Polymer Laboratories, Department of Polymer Science and Technology, Sri Krishnadevaraya University, Anantapur, Andhra Pradesh, India <sup>b</sup> Inorganic and Physical Chemistry Division, Indian Institute of Chemical Technology, Hyderabad, Andhra Pradesh, India

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## Synthesis and Characterization of Glycidyl Azide Polymer with Enhanced Azide Content

**Y. Murali Mohan**

**K. Mohana Raju**

Synthetic Polymer Laboratories, Department of Polymer Science and Technology, Sri Krishnadevaraya University, Anantapur, Andhra Pradesh, India

**B. Sreedhar**

Inorganic and Physical Chemistry Division, Indian Institute of Chemical Technology, Hyderabad, Andhra Pradesh, India

*The present study reports the preparation of glycidyl azide polymer with enhanced azide content. This process involves the cationic ring-opening polymerization of epichlorohydrin (ECH) using borontrifluoride etherate (BF<sub>3</sub>-etherate) and 2,2-bis(bromomethyl)1,3-propane diol (BMPD) as initiator and co-initiators, respectively, followed by subsequent azidation of the product. For both the products, poly(epichlorohydrin)s (PECHs) and glycidyl azide polymers (GAPs) the substituted 1,3-propane diol units were characterized by spectroscopic as well as thermal analysis. Vapor pressure osmometer studies indicated that as the diol concentration increased in the polymerization the formed PECH molecular weight decreased. The spectral analysis indicates the presence of corresponding diol units in their polymeric chains. The differential scanning calorimetry and elemental analysis of the GAPs developed in this investigation indicated the presence of higher azide content in the polymer.*

**Keywords:** glycidyl azide polymer (GAP), poly(epichlorohydrin) (PECH), cationic ring-opening polymerization, azidation, azide content

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Address correspondence to K. Mohana Raju, Synthetic Polymer Laboratories, Department of Polymer Science and Technology, Sri Krishnadevaraya University, Anantapur 515003, Andhra Pradesh, India. E-mail: krmrmoan@yahoo.com

## INTRODUCTION

There has been considerable interest in developing new propellant binders and oxidizers for solid propellants that not only provide high energy but also give better safety characteristics during processing [1–2]. The high-energy solid propellants are composite materials, containing a polymeric binder, high-energy additives (oxidizers), curing agents, burning rate modifiers, plasticizers, and so on [1]. The worldwide accepted work horse power propellant binder is hydroxy terminated poly(butadiene) (HTPB), which is an inert binder suitable to explosive formulations for air-blast and underwater applications [1,3]. But it is quite difficult to produce high performance cast-cured explosives for metal acceleration [3]. The strategy to change the fabrication method from cast-cure to extrusion or pressing helps in reducing the quantity of inert binder required in the formulations. Inclusion of explosophores (energetic functional groups), such as azido, nitro and fluoramines improves not only the internal energy of the propellant formulations but also the overall performance of the propellants [3]. New energetic binders were developed worldwide in the last two decades, including azide functional polymers like glycidyl azide polymer (GAP) [4–11], poly[3,3-bis(3-azidomethyl)oxetane] poly(BAMO) [12–14], poly[(3-azidomethyl)methyloxetane] poly(AMMO) [15–17]; nitrate polyethers like poly[(3-nitratomethyl)-3-methyloxetane] poly(NIMMO) [18], poly(glycidyl nitrate) poly(GLYN) [19]; polyvinyl-nitrates [20–21], fluoropolymers [22–23], N,N-bonded epoxy functional polymers [24–25] and nitrated poly butadienes [18] and so on, offering such promising characteristics to the propellant systems.

Among all the propellant binders, glycidyl azide polymer (GAP) or poly(glycidyl azide) is the most important and promising candidate, which is a low molecular weight [ $\approx 2000$  binder,  $\approx 500$  plasticizer] liquid pre-polymer having hydroxyl terminated telechelic polyether main chain with azidomethyl pendant groups [10–11]. Glycidyl azide polymers have created a new strategy due to their excellent properties, such as high positive heat of formation [26], low detonation sensitivity, low glass transition temperature, low viscosity, high density, and good compatibility with high energetic oxidizers [27].

GAP was first reported by E. J. Vandenberg in 1972, by reaction of poly(epichlorohydrin)triol (PECH-triol) with sodium azide in dimethylformamide [4]. Ampleman synthesized a diazido terminated glycidyl azide energetic plasticizer in two steps, first by converting the PECH-diols to PECH-(OTs)<sub>2</sub> and then following azidation reaction with sodium azide in DMF [5]. Energetic hydroxyl terminated aliphatic polyethers having pendant alkyl azide groups [ $(-\text{CH}_2)_n\text{N}_3$ ]

were developed by M. B. Frankel and E. Flanagan [6]. E. Ahad developed a direct process for the preparation of low molecular weight glycidyl azide polymer [7–8]. G. Ampleman reported an increased functionality of glycidyl azide polymer [9].

In most of the aforementioned processes as well as in the authors' previous reports, glycidyl azide polymer was prepared by azidation of PECH containing diol units in the polymeric chain, which itself was obtained by cationic ring-opening polymerization of epichlorohydrin, with  $\text{BF}_3$ -etherate as catalyst and diols as co-catalysts [10–11,28–33]. Therefore, after the azidation of PECH with sodium azide the GAP obtained contains somewhat smaller amount of diol units. In contrast to this, the present investigation provides a simple approach to improve the azide content in GAP by employing a new diol, 2,2-bis(bromomethyl)1,3-propane diol (BMPD) in the PECH synthesis. The present work describes the synthesis of glycidyl azide polymer having high azide content. The improved azide content in the GAP is confirmed by elemental and differential scanning calorimeter (DSC) analysis.

## EXPERIMENTAL

### Materials

Epichlorohydrin (ECH) and dichloromethane (DCM) were purified by normal distillation; borontrifluoride etherate ( $\text{BF}_3$ -etherate) and dimethylformamide (DMF) were distilled under reduced pressure. All the aforementioned reagents and solvents were kept under nitrogen atmosphere. Sodium azide ( $\text{NaN}_3$ ) having purity >98% was used as received. All the chemicals were purchased from S. D. Fine-Chem Limited (Mumbai, India). 2,2-bis(bromomethyl)1,3-propane diol (BMPD) was purchased from Sigma-Aldrich (Germany). The nitrogen gas was purified by passing through pyrogallol solution and calcium chloride towers.

### Synthesis of Poly(epichlorohydrin) [29–30]

The synthesis of poly(epichlorohydrin) was carried out in a three-necked round flask connected to a nitrogen inlet, a calcium chloride guard tube, and an efficient magnetic stirring bar. In a typical reaction, 5.307 g of 2,2-bis(bromomethyl)1,3-propanediol was dissolved in 100 ml of dichloromethane taken in the flask and then 0.5 ml of borontrifluoride etherate was introduced and stirred well for 30 min. To this polymerization mixture, 18.750 g of epichlorohydrin dissolved in 30 ml

**TABLE 1** Synthetic Details of Poly(epichlorohydrin) and Glycidyl Azide Polymer

| Polymer code | ECH mol (gms) | BMPD mol (gms)  | PECH yield (%) <sup>a</sup> | Molecular weight ( $\bar{M}_n$ ) <sup>b</sup> |     |
|--------------|---------------|-----------------|-----------------------------|---|-----|
|              |               |                 |                             | PECH  | GAP |
| PECH 1       | 0.202 (16.84) | 0.0202 (5.307)  | 97                          | 810   | 925 |
| PECH 2       | 0.202 (16.84) | 0.03039 (7.960) | 96                          | 680   | 815 |
| PECH 3       | 0.202 (16.84) | 0.0405 (10.614) | 89                          | 540   | 610 |

<sup>a</sup>Polymer yield with 0.5 ml of borontrifluoride etherate initiator; <sup>b</sup>Molecular weight ( $\bar{M}_n$ ) determined by VPO.

of chloroform was added drop wise for 30–60 min. The reaction was carried out at 0°C for 6 h and left overnight under stirring at room temperature. The reaction was then quenched with 50 ml of saturated sodium chloride solution. The DCM layer was separated and washed several times with hot distilled water to remove the traces of initiator and un-reacted diol. After distilling the DCM, the distillation was continued under vacuum to remove the un-reacted epichlorohydrin, in order to get pure PECH. The details of reaction conditions are presented in Table 1.

### Synthesis of Glycidyl Azide Polymer [29–30]

It is well known that the halogenic polyethers are converted into their corresponding azido polyether derivatives by reaction with sodium azide, in aprotic solvents such as dimethyl formamide (DMF), dimethyl acetate (DMAc), and dimethyl sulfoxide (DMSO) [10–11,33–36]. In a typical conversion reaction, 10 g of PECH dissolved in dimethyl formamide was taken in a 250 ml three-necked flask equipped with a mechanical stirrer and a reflux condenser with calcium chloride guard tube. The solution was heated upto 120°C in an oil bath and then 10 g of sodium azide was slowly added to the reaction mixture and continued the stirring for 10 h at this temperature. After completion of the reaction time the reaction mixture was cooled to room temperature and followed the purification process as per reported in the literature to get GAP [2].

### Characterization

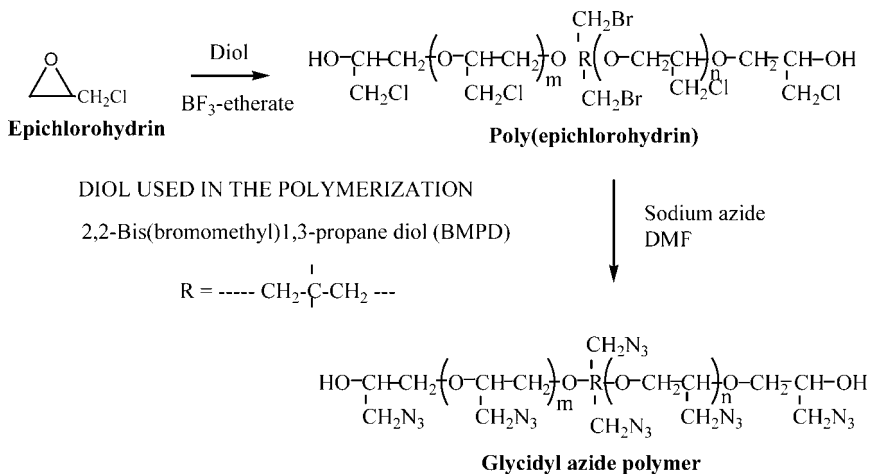
The UV spectra of polymers were measured with a Shimadzu 160 A UV spectrophotometer using very dilute solutions in chloroform. Infrared

spectra of polymers were recorded using a PERKIN ELMER pc 16 FTIR spectrometer and scanned in the range of 500–4500  $\text{cm}^{-1}$ .  $^1\text{H-NMR}$  spectra of polymers were measured using a JEOL GSX 400 MHz NMR spectrometer in  $\text{CDCl}_3$  solvent using tetramethylsilane as internal standard. Differential scanning calorimetry (DSC) of polymers was performed using METTLER TOLEDO STAR<sup>e</sup> System at a heating rate of 5°C/min under 30 ml/min of nitrogen flow. Thermal analysis of polymers was performed using METTLER TOLEDO STAR<sup>e</sup> System at a heating rate of 5°C/min under 30 ml/min of nitrogen flow. The molecular weight measurements were carried out with waters GPC using RI as detector and PMMA standards.

## RESULTS AND DISCUSSION

Epichlorohydrin polymerizations were normally conducted using borontrifluoride etherate as catalyst in presence of small amounts of diols as co-catalysts [28–33]. Various diols, including ethylene glycol (EG), 1,4-butanediol (BD), and 4,4'-azobis(4-cyanopentanol) (ACPO) serve effectively for this purpose as co-catalysts [37]. The polymerization of epichlorohydrin using  $\text{BF}_3$ -etherate/diol initiating system follows the activated monomer mechanism [38]. In addition to this, the present authors' reports also revealed that ethylene glycol, propylene glycol (PG), diethylene glycol (DEG), hexane diol (HD), cyclohexane diol (CHD), resorcinol (RS), and poly(ethylene glycol)s (PEGs) also serve effectively as co-catalysts [29–30]. The polymers synthesized by the aforementioned methods contain the diol units linked together with monomeric units in the polymeric chains. In general, low molecular weight poly(epichlorohydrin)s were used as precursors in the preparation of glycidyl azide polymers, which are considered as prominent candidates for propellant binders. The azidation reaction of PECH with sodium azide results in GAP. If that precursor contains other than ECH repeating units, that is, diol units in the polymeric chain, the total azide content decreases in the formed GAP.

The present study employed a different diol, namely 2,2-bis(bromomethyl)1,3-propane diol as co-catalyst, for the ring-opening polymerization of epichlorohydrin. All the polymerizations were carried out in the presence of borontrifluoride etherate as catalyst. The polymers obtained in this process contain 2,2-bis(bromomethyl)1,3-propane diol unit in the center and the ECH repeating units on both ends of the chain and have a representative polymer structure, PECH-BMPD-PECH. The three grades of PECHs prepared were converted into their corresponding azidated polymers, namely, GAP-AMPD-GAP polymers. The azidation reaction of PECHs containing BMPD units was

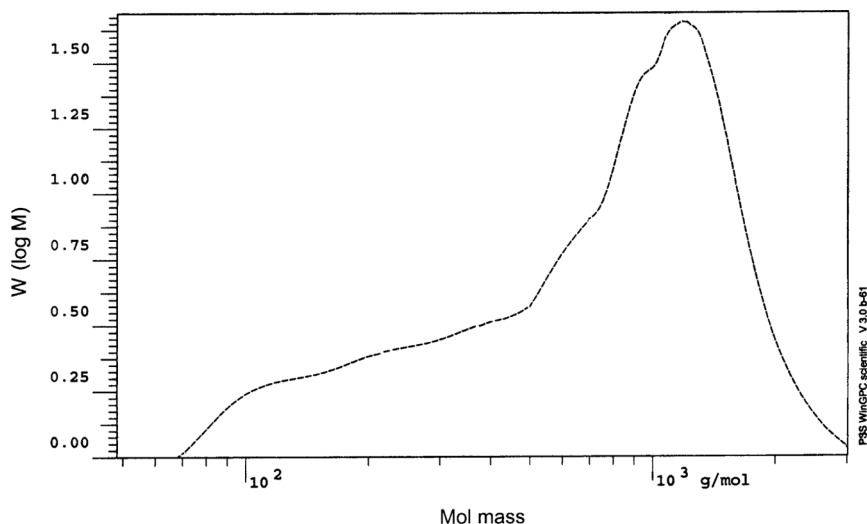


**SCHEME 1** Glycidyl azide polymer formation.

achieved by reacting PECHs with sodium azide for 10 h at 120°C. A typical schematic representation of the preparation of GAP having enhanced azide content is depicted in Scheme 1.

As the concentration of diol increases from 10 to 20 mol%, the molecular weight of the PECH decreases from 810 to 540 g/mol. With increase diol concentration in the polymerization reaction, the initiating oxonium ions have increased, thereby decreasing the average chain length of the polymer, that is, molecular weight of the polymer. The GAPs obtained in this investigation are found to have molecular weight ( $\bar{M}_n$ ) in between 925 to 610 g/mol. The synthetic details of the PECHs and GAPs are given in Table 1. Further, it is also found that either the molecular weight or the hydroxyl content of the polymer has no effect on the azidation reaction. For example, PECH 1 ( $\bar{M}_n = 810$ ; hydroxyl value = 114.2 mg of KOH/gm) on azidation gives GAP ( $\bar{M}_n = 925$ ; hydroxyl value = 113.4 mg of KOH/gm). Some reports have indicated that the azidation of rubbery PECH with sodium azide in presence of a base leads to degradation process resulting in decreased molecular weight of the GAP [39–40]. The gel permeation chromatograms of GAP are presented in Figure 1, and PECH 1 and GAP 1 containing 10% diol shown is having molecular weight distribution > 1.9.

The formation of polymers was confirmed by different analytical techniques like UV, IR,  $^1\text{H-NMR}$ , elemental, differential scanning calorimeter (DSC), and thermogravimetric analyzer (TGA).



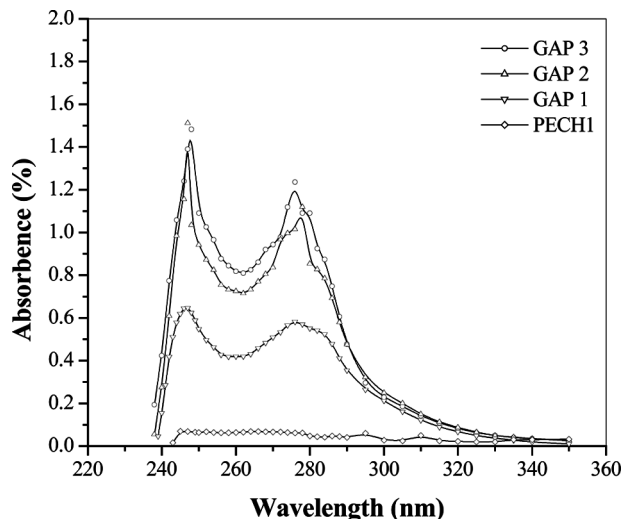
**FIGURE 1** Gel permeation chromatograph of GAP 1.

### Spectral Analysis

The PECHs and the corresponding azidated polymers (GAPs) were characterized from their UV, IR, and  $^1\text{H-NMR}$  spectral analysis [10–11,41]. The UV spectra of PECHs and GAPs are presented in Figure 2. The UV spectra of GAPs shows two absorption peaks one at 248 nm and the other at 278 nm corresponding to the resonance of nitrogen bonds  $-\text{CH}_2-\text{N}^--\text{N}=\text{N}^+$  and  $-\text{CH}_2-\text{N}^--\text{N}^+\equiv\text{N}$  of the azide group of the GAP [10–11,29–30], whereas its precursors PECHs have not showed any absorbance in the UV region.

The IR spectra of the PECHs have shown the characteristic peaks at  $748\text{ cm}^{-1}$ ,  $1190\text{ cm}^{-1}$ ,  $2845\text{ cm}^{-1}$ , and  $3380\text{ cm}^{-1}$ , corresponding to  $-\text{CH}_2\text{Cl}$  group, C–O–C polyether chain, methylene groups, and  $-\text{OH}$  groups, respectively [10–11,29–30]. In addition to the aforementioned peaks PECHs have shown another characteristic peak at  $703\text{ cm}^{-1}$ , belonging to  $\text{CH}_2-\text{Br}$  of BMPD indicating the incorporation of BDPM units in the polymeric chain [41]. The formation of azide groups in the GAPs is also clearly noticed in their IR spectra. In the IR spectra of the GAPs, the peaks corresponding to  $\text{CH}_2\text{Cl}$  and  $\text{CH}_2\text{Br}$  groups at  $748\text{ cm}^{-1}$  and  $703\text{ cm}^{-1}$ , respectively, are completely absent and additional peaks corresponding to azide groups are present at  $2100\text{ cm}^{-1}$  and  $1280\text{ cm}^{-1}$ , indicating the complete replacement of chlorine and bromine atoms in the PECHs by azide groups forming GAPs [10–11,29–30]. The IR spectra of PECHs containing BDPM





**FIGURE 2** UV spectra of poly(epichlorohydrin) and glycidyl azide polymers.

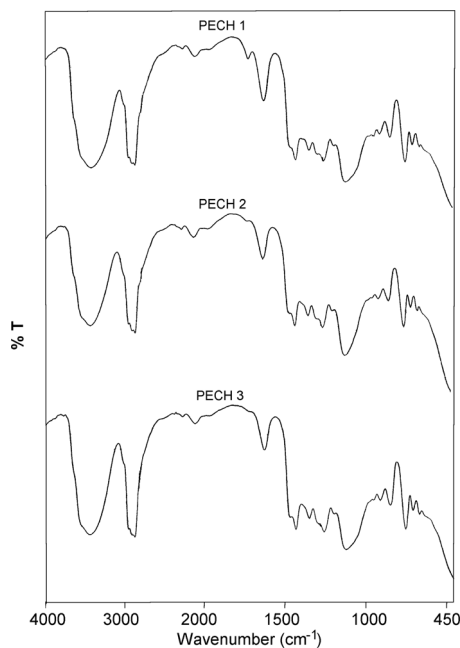
units and GAPs containing AMPD units are presented in Figures 3 and 4, respectively.

The  $^1\text{H-NMR}$  spectral analysis also supports the formation of polymers [29–30,41–42]. In the  $^1\text{H NMR}$  spectrum of PECH 1, containing BDPM units, the peaks observed are at 3.5 ppm due to  $\text{CH}_2\text{Br}$  protons of the BDPM units, 3.6 ppm due to  $\text{CH}_2\text{Cl}$  protons of PECH pendants and 3.7 ppm due to the protons of  $\text{CH}_2$ ,  $\text{CH}$  groups of the polyether main chain of PECH. The  $^1\text{H-NMR}$  spectrum of GAP 1, showed the peaks at 3.25 ppm corresponding to methylene protons of the pendant azidomethyl groups ( $-\text{CH}_2\text{N}_3$ ) of GAP and at 3.7 ppm belonging to the methylene protons of polyether main chain of GAP. The  $^1\text{H-NMR}$  spectra of PECH 1 and GAP 1 are presented in Figure 5.

The spectral analysis clearly demonstrates the formation of the poly(epichlorohydrin) containing BMPD units by the ring opening polymerization of epichlorohydrin and subsequent azidation of PECH with sodium azide replacing completely the chlorine and bromine atoms by azide groups. Further, the spectral analysis also confirms the presence of BMPD units in PECH and 2,2-bis(azidomethyl)-1,2 propane diol (AMPD) in GAP chains along with secondary hydroxyl end groups.

## Thermal Studies

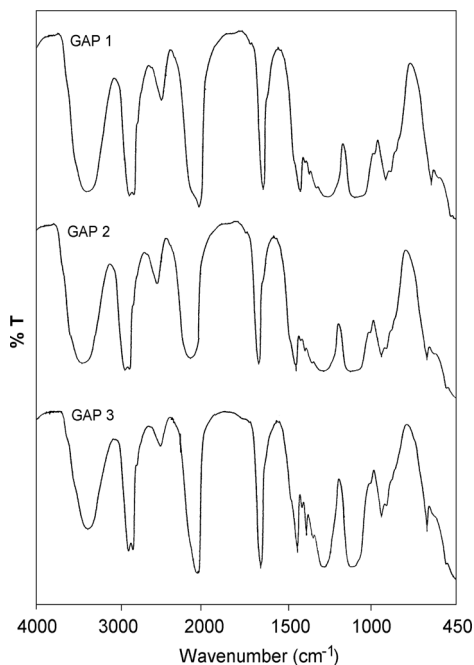
The polymeric binders play an important role in the combustion of solid propellants. Therefore it is necessary to study the thermal



**FIGURE 3** IR spectra of poly(epichlorohydrin)s.

decomposition behaviour of polymeric propellant binders, which are finding applications in space technology. In view of the aforementioned applications it become necessary to carry out the DSC and TGA analysis of the glycidyl azide polymers containing AMPD units in order to know their competitive thermal stability and decomposition modes.

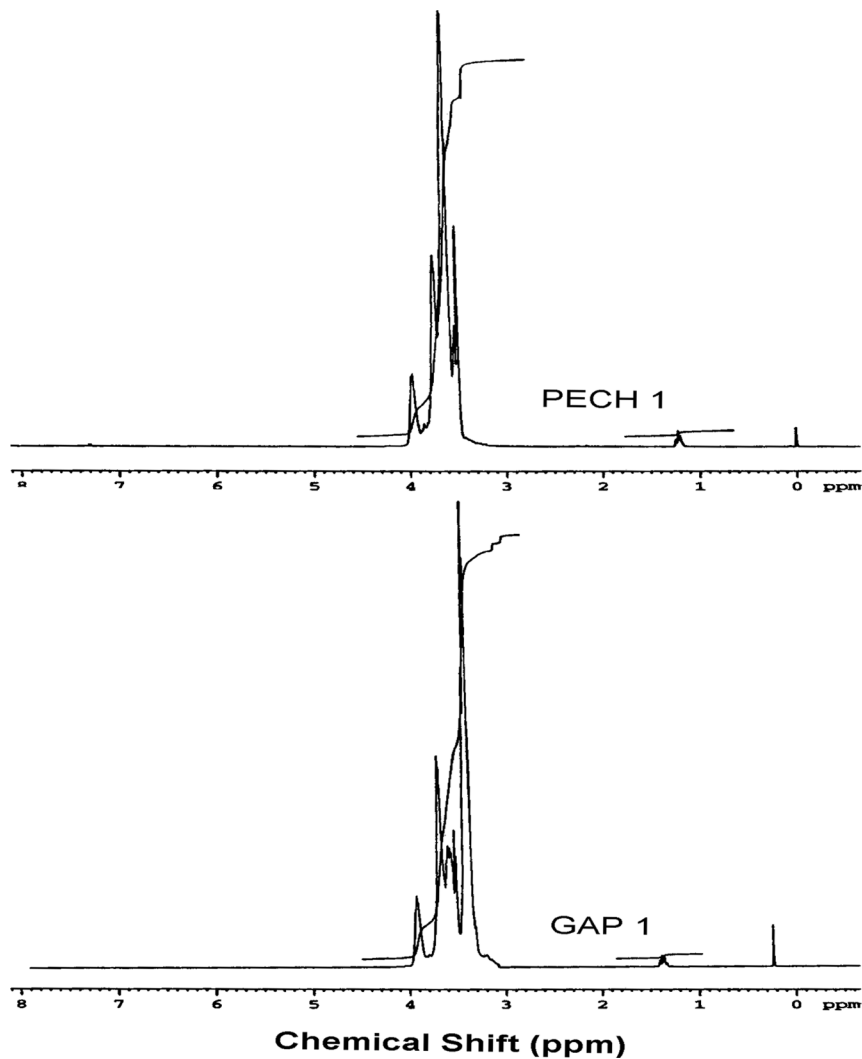
A representative DSC thermogram of GAP 1 containing AMPD units is presented in Figure 6. In DSC curves of glycidyl azide polymers containing AMPD units, it is noticed that there are no decomposition peaks upto 190°C, and the onset of decomposition of the polymers starts only above 190°C. A single exothermic peak in all the DSC curves of the glycidyl azide polymers is found in between 242°C and 244°C, similar to pure glycidyl azide polymer [10–11,29–30]. This exothermic peak is due to the elimination of nitrogen molecules by the scission of the azide groups of GAP [10–11,26]. The peak decomposition temperature of these polymers slightly increased due to increase of structurally hindered azido groups of AMPS. Further, the exothermic behavior of the GAPs can be explained from their heat of decomposition values ( $\Delta H$ ) [11]. These decomposition values slightly



**FIGURE 4** IR spectra of glycidyl azide polymers.

increased as the AMPD content increased in the polymeric chains, because they contain a higher number of azide groups, which are responsible for higher amounts of heat release. It is an important conclusion that should be made because the obtained heat of decomposition values (1841–1895 J/g) is quite higher than glycidyl azide polymers. Pure GAP has the heat of decomposition of about 1828 J/g [11]. Thus, the glycidyl azide polymers prepared in this investigation have shown higher decomposition values indicating the presence of higher number of azide groups in the polymeric chains.

The TGA curves of glycidyl azide polymers containing AMPD units, demonstrates two-step weight loss pattern [26]. The first degradation step starts above 207°C and the second step starts around 290°C. The first degradation step is assigned to the azide groups of GAP, because the pendant azide group of GAP is sensitive to thermal cleavage more than any other group present in the structure of GAP. The first decomposition is the results of the nitrogen elimination from the azide group of the polymers by intramolecular cyclization as well as intermolecular crosslinking leading formation of nitrine or imines as pendants in the polymeric chains [10]. The thermal decomposition of



**FIGURE 5**  $^1\text{H}$ -NMR spectra of PECH and GAP.

azide groups of GAPs was clearly explained in detail by high temperature FTIR and infrared laser-induced decomposition studies [10–11,43–44]. The maximum decomposition rate temperature ( $T_{\text{max}}$ ) of azide groups is observed around 230–240°C for these polymers, and this temperature increases with increase in the amount of AMPD units present in the polymeric chains. The  $T_{\text{max}}$  increased from 229 to

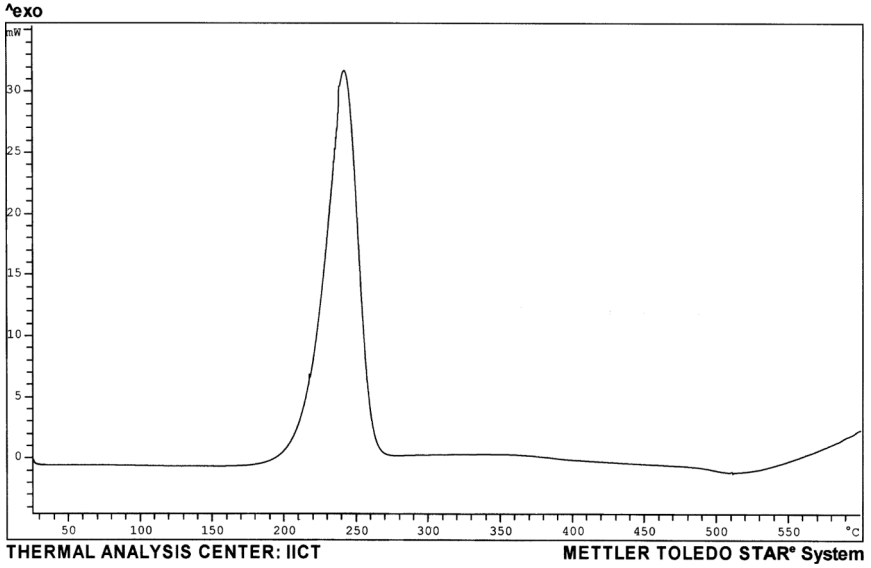


FIGURE 6 DSC curve of GAP 1.

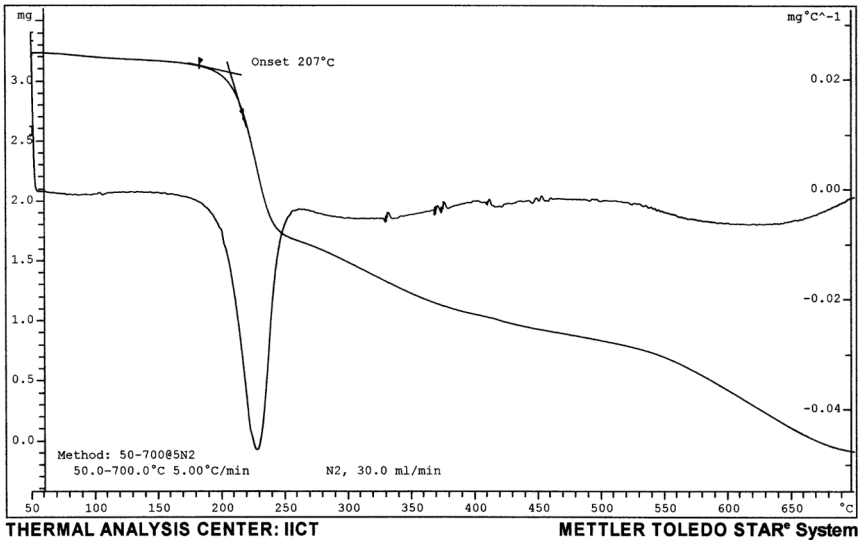


FIGURE 7 TGA curve of GAP 1.

**TABLE 2** Thermal Analysis of Poly(epichlorohydrin) and Glycidyl Azide Polymers

| Polymer code | TGA                                  |                                     | DSC                                 |                             |
|--------------|--------------------------------------|-------------------------------------|-------------------------------------|-----------------------------|
|              | Onset decomposition temperature (°C) | Peak decomposition temperature (°C) | Peak decomposition temperature (°C) | Heat of decomposition (J/g) |
| PECH 1       | 242                                  | 285                                 | 319                                 | —                           |
| GAP 1        | 207                                  | 229                                 | 242                                 | 1841.42                     |
| GAP 2        | 208                                  | 234                                 | 243                                 | 1863.50                     |
| GAP 3        | 225                                  | 241                                 | 244                                 | 1895.95                     |

241°C as the diol content used increased from 10 to 20%. The second weight loss region represents the decomposition of the main chain of polyether. A representative TGA thermogram of GAP 1 is presented in Figure 7, where the PECH containing BMPD units showed a single step decomposition belonging to main polyether chain of PECH. The onset decomposition temperature and peak decomposition temperatures are noted as 242.91°C and 285°C, respectively. Thermal analysis of the polymers is presented in Table 2.

### Nitrogen Content

The nitrogen content of the polymers was determined by elemental analyzer as well as by DSC analysis. It is found that GAPs obtained in the present investigation have shown a higher percentage of nitrogen content, in between 42.54–43.80%, when compared to pure (42.23%) [11] (Table 3). The increment in the azide content in the glycidyl azide polymers developed in this study is due to the presence of extra azido groups belonging to initiative diol units presented in the polymer.

**TABLE 3** Nitrogen Content of Glycidyl Azide Polymer

| Polymer code          | Instrumental | DSC <sup>b</sup> |
|-----------------------|--------------|------------------|
| Pure GAP <sup>a</sup> | 42.23        | —                |
| GAP 1                 | 42.45        | 42.54            |
| GAP 2                 | 42.92        | 43.05            |
| GAP 3                 | 43.65        | 43.80            |

<sup>a</sup>From Reference [11]; <sup>b</sup>calculated the nitrogen content by comparing the  $\Delta H$  values of the polymers with pure GAP.

## CONCLUSION

The glycidyl azide polymers developed in this investigation contain higher amounts of azide groups, prepared by a two-step process involving the polymerization of epichlorohydrin using  $\text{BF}_3$ -etherate and 2,2-bis(bromomethyl)1,3-propane diol as initiator and co-initiators by cationic ring-opening polymerization and subsequent azidation with sodium azide. The synthesized poly(epichlorohydrin)s containing BMPD units and glycidyl azide polymers containing 2,2-bis(azidomethyl)-1,3-propane diol units were structurally characterized by UV, IR, and  $^1\text{H-NMR}$  spectroscopy. The TGA and DSC analysis of these polymers indicates the decomposition behavior is similar to pure GAP. The elemental and DSC analysis showed the presence of nitrogen content  $>42.50\%$ .

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