

Synthesis, Spectral and DSC Analysis of Glycidyl Azide Polymers Containing Different Initiating Diol Units

Y. Murali Mohan, M. Padmanabha Raju, and K. Mohana Raju

Synthetic Polymer Laboratories, Department of Polymer Science and Technology, Sri Krishnadevaraya University, Anantapur 515 003, AP, India

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ABSTRACT: Glycidyl azide polymers (GAPs), containing different diol units, were prepared by treating the corresponding poly(epichlorohydrin)s (PECHs) with sodium azide in DMF solvent at 110°C for 8–10 h. The poly(epichlorohydrin)s containing different diol units were synthesized by the polymerization of epichlorohydrin using borontrifluoride etherate as initiator in the presence of a small amount of low molecular weight diols. The formation of these PECHs was confirmed by IR spectroscopy. The nature of terminal hydroxyl group present in the polymer chain was confirmed by proton NMR spectroscopy. The structure

of GAPs containing different initiating diol units was confirmed by UV, IR, and proton NMR spectral analysis. Thermal properties of the GAPs were evaluated using differential scanning calorimetry; the stabilities and glass-transition temperatures of the GAPs varied according to the initiating diol unit present in the polymer chains. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 93: 2157–2163, 2004

Key words: glycidyl azide polymer (GAP); poly(epichlorohydrin) (PECH); ring-opening polymerization; glass transition; thermal properties

INTRODUCTION

Energetic binders, consisting of polymers and plasticizers, are finding increased use in cast-cured polymer-bonded explosives and cast-composite rocket propellants.¹ Energetic binders are considered as crosslinked polymers that provide a matrix in which to bind the explosive ingredients together with particulate particle oxidizer, burning rate catalyst, plasticizer, and so forth, resulting in a tough elastomeric three-dimensional network structure capable of absorbing and dissipating energy from hazardous stimuli, lending itself well to insensitive munitions (IM) applications.¹

Within the last two decades new initiatives in research work have been aimed at developing materials with better specific impulsive properties and chlorine-free propellants. Attention has been focused particularly on several energetic polymers including azide polymers; glycidyl azide polymers (GAPs)^{2–10}; poly(3-azidomethyl, 3-methyl oxetane) [poly(AMMO)]^{11–14}; poly[3,3-bis (azidomethyl) methyl oxetane] [poly(BAMO)]^{13–16}; poly(3-nitromethyl-3-methyl oxetane) [poly(NMMO)]¹⁵; poly[3,3-(nitratomethyl) methyl oxet-

ane] [poly(NIMMO)]¹⁷; poly(glycidyl nitrate) [poly(G-LYN)]^{17,18}; and corresponding copolymers^{5,6,14–16,19} to fulfill the above requirements. Azido polymers are potential candidates for the preparation of propellants and contain the energetic azide pendent groups.⁸ Glycidyl azide polymer (GAP) or poly(glycidyl azide) (PGA) is one of the most recognized and prominent azide polymer, characterized by a low molecular weight hydroxyl-terminated difunctional liquid prepolymer with pendent azidomethyl groups on the polyether main chain. In fact GAP is a high energy potential material with a high positive heat of formation (+957 kJ/kg) and low detonation sensitivity properties, and is considered both a monopropellant and a polymeric binder.^{2,3,8} GAP has a low glass-transition temperature ($T_g = -48^\circ\text{C}$), low viscosity (2.4×10^3 cps at 25°C), and high density compared to these same characteristics of other rocket propellant binders.^{2,3} In addition, GAP has good compatibility with all high-energy oxidizers.¹ Because of its superior properties GAP is used extensively as a high energetic binder-cum-plasticizer to increase burning and specific impulse of the propellants. Because of its adequate ability to function as a propellant binder/plasticizer, we have attempted to develop GAP-PEG-GAP triblock copolymers.²⁰

As part of an ongoing program the present work involves the preparation of GAPs containing various initiating diol units in the polymer chain. Formation of the GAPs was confirmed by spectral analysis. The ther-

Correspondence to: K. Mohana Raju (kmrmohan@yahoo.com).

mal stabilities and glass-transition temperatures of the developed GAPs were evaluated by DSC thermograms.

EXPERIMENTAL

Materials

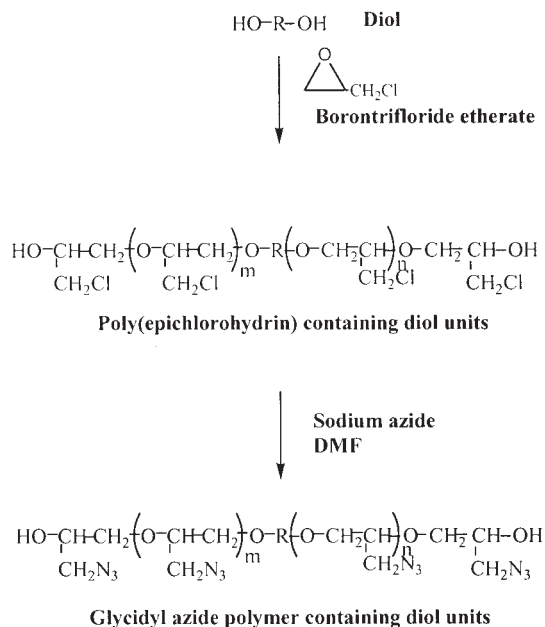
Epichlorohydrin, ethylene glycol (EG), propane-1,2-diol (PD), diethylene glycol (DEG), 2-methylpropane-2,4-diol [hexylene glycol (HG)], dimethylformamide, and dichloromethane were purchased from S.D. Fine Chemicals (Bombay, India) and purified following the standard methods of purification. 1,4-Cyclohexane diol (CHD) and resorcinol (RS) were purchased from Merck (Darmstadt, Germany) and used as received; borontrifluoride etherate (BF_3 -etherate) was purchased from Spectrochem (Bombay, India) and purified by vacuum distillation. Purified solvents and reagents were kept over molecular sieves. Nitrogen was purified by passing it through pyrogallol solution and calcium chloride towers.

Synthesis of poly(epichlorohydrin) (PECH)²¹

The ring-opening polymerization of epichlorohydrin was carried out in a 250-mL three-neck flask containing a magnetic needle, equipped with a calcium chloride guard tube, nitrogen line, and a dropping funnel. To the stirred solution of diol in dichloromethane, borontrifluoride etherate was added dropwise using a dropping funnel at room temperature, while passing nitrogen gas into the flask, and stirring was continued for 30 min. The reaction flask was then brought to 0°C using an ice-salt mixture. Epichlorohydrin dissolved in dichloromethane was slowly added to the reaction mixture drop by drop for 1 h; the reaction was continued for 4–5 h at the same temperature and then stirred overnight at room temperature. The reaction was quenched by adding 50 mL of distilled water. The polymer solution was separated from water and then treated with distilled water to remove unreacted diol and the initiator. The pure polymer was obtained by removing the solvent by vacuum distillation.

Preparation of glycidyl azide polymer (GAP)⁸

The PECH in dimethylformamide was introduced into a two-neck flask equipped with a condenser, a magnetic needle, and a calcium chloride guard tube. The reaction mixture was heated slowly until the polymer was dissolved in the solvent. To this reaction mixture, sodium azide (slight excess of molar ratio) was added slowly and the temperature was raised to 110°C. After 8–10 h of reaction time, the polymer solution was cooled to room temperature and filtered to remove the salts and the unreacted sodium azide. The filtered polymer solution was poured into distilled water where the polymer was



Scheme 1 Schematic representation of the preparation of glycidyl azide polymer containing diol units.

precipitated and separated out. The polymer was repeatedly washed with water until the washings were free from azide and chloride ions. The polymer was then dissolved in chloroform and dried over sodium sulfate. The solvent was removed by vacuum distillation to obtain the pure polymer.

The schematic representation of the above two reactions for the synthesis of GAP is depicted in Scheme 1.

Analysis of the polymers

The UV spectra of polymers were measured with a Shimadzu (Kyoto, Japan) 160A UV spectrophotometer using very dilute solutions in chloroform solvent. IR spectra of polymers were recorded a Perkin-Elmer 882 IR spectrophotometer (Perkin Elmer Cetus Instruments, Norwalk, CT). Proton NMR spectra of polymers were measured using a JEOL (Tokyo, Japan) GSX 400-MHz NMR spectrometer in CDCl_3 solvent, using tetramethylsilane as an internal standard. Differential scanning calorimetry (DSC) of polymers was performed by an Netzsch DSC 204 instrument (Netzsch-Gerätebau GmbH, Bavaria, Germany) at a heating rate of 10°C/min under nitrogen flow. The molecular weight of the polymers was determined by end-group analysis following a conventional acetylation method using pyridine as catalyst.

RESULTS AND DISCUSSION

Epichlorohydrin polymerization in the presence of a small amount of initiative diol compounds²¹

The cationic ring-opening polymerization of epichlorohydrin, by combination of borontrifluoride ether-

TABLE I
Synthetic Details of Poly(epichlorohydrin)s Containing Different Diol Units

Polymer code	Epichlorohydrin (g)	Diol (g)	Polymer yield (%)	Initiating diol identification in IR analysis	Initiating diol identification in UV spectra
PECH EG	18.75	1.250 (EG)	95.00	No peak is found	No peak found
PECH PD	18.75	1.545 (PD)	93.80	No peak is found	No peak found
PECH DEG	18.75	2.150 (DEG)	94.40	No peak is found	No peak found
PECH HG	18.75	2.394 (HG)	88.00	No peak is found	No peak found
PECH CHD	18.75	2.353 (CHD)	85.85	No peak is found	No peak found
PECH RS	18.75	2.230 (RS)	85.00	Found a peak around 1700 cm^{-1}	A peak is observed at 290 nm attributed to resorcinol aromatic system

ate/low molecular weight diol initiating system, followed the activated monomer (AM) mechanism as reported for ethylene glycol or butane diol.^{4,21–25} To determine the effect of different diol units on the properties of GAP, different initiative diol units were introduced into the PECH polymer chain by polymerizing epichlorohydrin with borontrifluoride etherate in the presence of initiative diols. The synthetic details of the preparation of PECHs are given in Table I. These polymerizations gave liquid resins of low molecular weights, containing hydroxyl functional groups as terminal ends. As shown in Table I, the low molecular weight and linear diol produced high polymer yields when compared to high molecular weight or cyclic diol. The molecular weights of the poly(epichlorohydrin)s are in the range of 850–980 g/mol.

The diols used in the polymerization of epichlorohydrin were incorporated into the polymeric chains and confirmed by IR spectroscopy as shown in Figure 1. The IR spectra of all the polymers showed similar stretching peaks^{2,3} at 3450, 1190, and 745 cm^{-1} , corresponding to OH, C—O—C, and CH_2Cl functional groups, respectively. However, there were small variations for the peaks corresponding to $-\text{CH}$, $-\text{CH}_2$, and $-\text{CH}_3$ in the IR spectra around 2900 cm^{-1} . From this

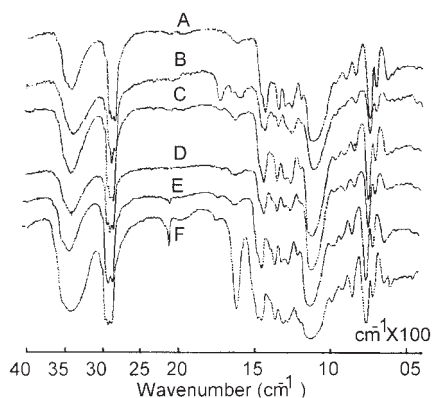


Figure 1 IR spectra of poly(epichlorohydrin)s: (A) PECH EG; (B) PECH PD; (C) PECH DEG; (D) PECH HG; (E) PECH CHD; (F) PECH RS.

observation it was not possible to determine which diol unit was present in the polymeric chains because there were no other peaks corresponding to diol units found in the IR spectra of polymers, except in the case of PECH (RS), where a peak corresponding to the aromatic ring system was found.²⁶

According to the activated monomer mechanism, the entire diol is consumed in the initial stages of polymerization without having any residual diol to be attached as terminal end in the polymer chain. To understand this behavior, it is important to ascertain the nature of the terminal hydroxyl groups present in the polymer chains. To establish the nature of the terminal hydroxyl group, ¹H-NMR spectroscopy was used. The ¹H-NMR spectrum of triethylchloroacetylisocyanate derivation of the product of GAP (EG) showed the characteristic peaks at 5.2 ppm, corresponding to secondary hydroxyl groups, and no peaks that corresponded to primary hydroxyl groups²⁶ in Figure 2. This indicates that the hydroxyl groups at the terminal ends were secondary in nature.

Preparation of glycidyl azide polymer

The novel telechelic hydroxyl-terminated glycidyl azide polymers, having different diol units in the polymer chains, were prepared by reacting the corresponding poly(epichlorohydrin)s with sodium azide in dimethylformamide at 110°C for 8–10 h. The polymers were amber/dark colored liquids having molecular weights between 900 and 1100 g/mol.

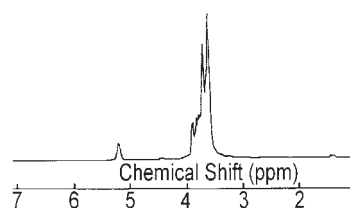


Figure 2 ¹H-NMR spectra of PECH EG derivation with trichloroacetylisocyanate.

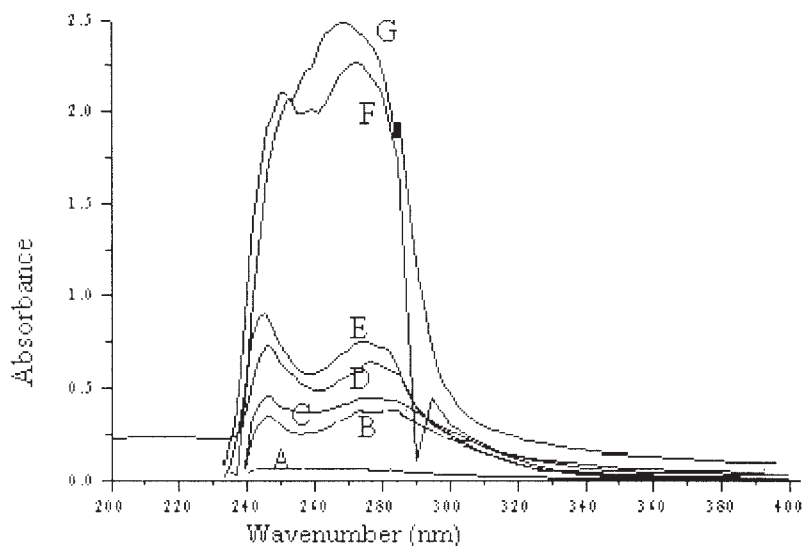


Figure 3 UV spectra of poly(epichlorohydrin) and glycidyl azide polymers: (A) PECH EG; (B) GAP DEG; (C) GAP HG; (D) GAP EG; (E) GAP PD; (F) GAP CHD; (G) GAP RS.

Spectral analysis

The formation of glycidyl azide polymers was confirmed from the characteristic peaks obtained in UV and IR spectra. The UV and IR spectra of the polymers are presented in Figures 3 and 4, respectively. The UV spectra of glycidyl azide polymers show two peaks at 247 and 278 nm, attributed to resonance of nitrogen bonds of the azide group of the polymer.^{2,3} The IR spectra of GAPs show the main characteristic peaks at 1280 and 2080 cm^{-1} , corresponding to formation of the azide group in the polymer chain, and with total disappearance of the CH_2Cl peak at 746 cm^{-1} .^{2,3} The presence of the strong prominent peaks corresponding to $\text{CH}_2\text{—N}_3$ groups and complete disappearance of the CH_2Cl peak indicates that all the chlorine atoms in the PECH were replaced by the azide groups in the azidation reactions.

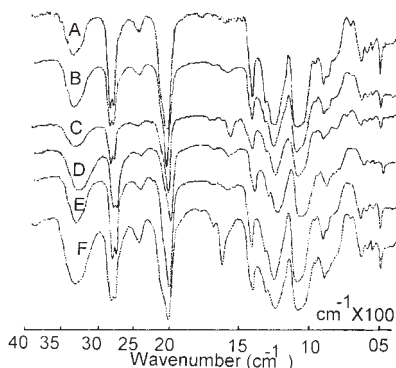


Figure 4 IR spectra of glycidyl azide polymers: (A) GAP EG; (B) GAP PD; (C) GAP DEG; (D) GAP HG; (E) GAP CHD; (F) GAP RS.

The glycidyl azide polymers containing the different initiated diol units were identified from their $^1\text{H-NMR}$ spectra²⁶ as shown in Figure 5. The common peaks observed for all the GAPs^{2,3} were around (δ) 3.8 ppm (CH_2 , CH protons of polyether main) and 3.4 ppm (CH_2N_3 proton). In addition to the above peaks, the characteristic peaks corresponding to the protons of the different diol units were observed in their spectra: the peaks²⁶ at (δ) 1.1–1.2 ppm, attributed to CH_3 protons of propane diol; 1.2–1.9 ppm, attributed to CH_3 and CH_2 protons of hexylene diol; 1.1–2.1 ppm, attributed to $-\text{CH}$ and $-\text{CH}_2$ protons of cyclohexane diol; and 6.4–8.0 ppm, corresponding to the protons of the resorcinol diol in the polymeric chains of GAPs. These peak positions in the NMR spectra of glycidyl azide polymers strictly corroborate the UV and IR analyses for the presence of the diol units in the polymer chains and the formation of glycidyl azide polymer.

The spectral studies are obviously a measurement for the formation of glycidyl azide polymers from their corresponding poly(epichlorohydrin)-containing diol units. The conversion reactions occurred without affecting either the terminal hydroxyl end groups or the molecular weight of the polymers.

Thermal studies

Thermal decomposition of the propellant binders plays a crucial role in the combustion of the composite solid propellants, and so it is necessary to study the thermal decomposition of the GAPs. To ascertain the decomposition temperatures of the polymers, the DSC thermograms were recorded. A main single exother-

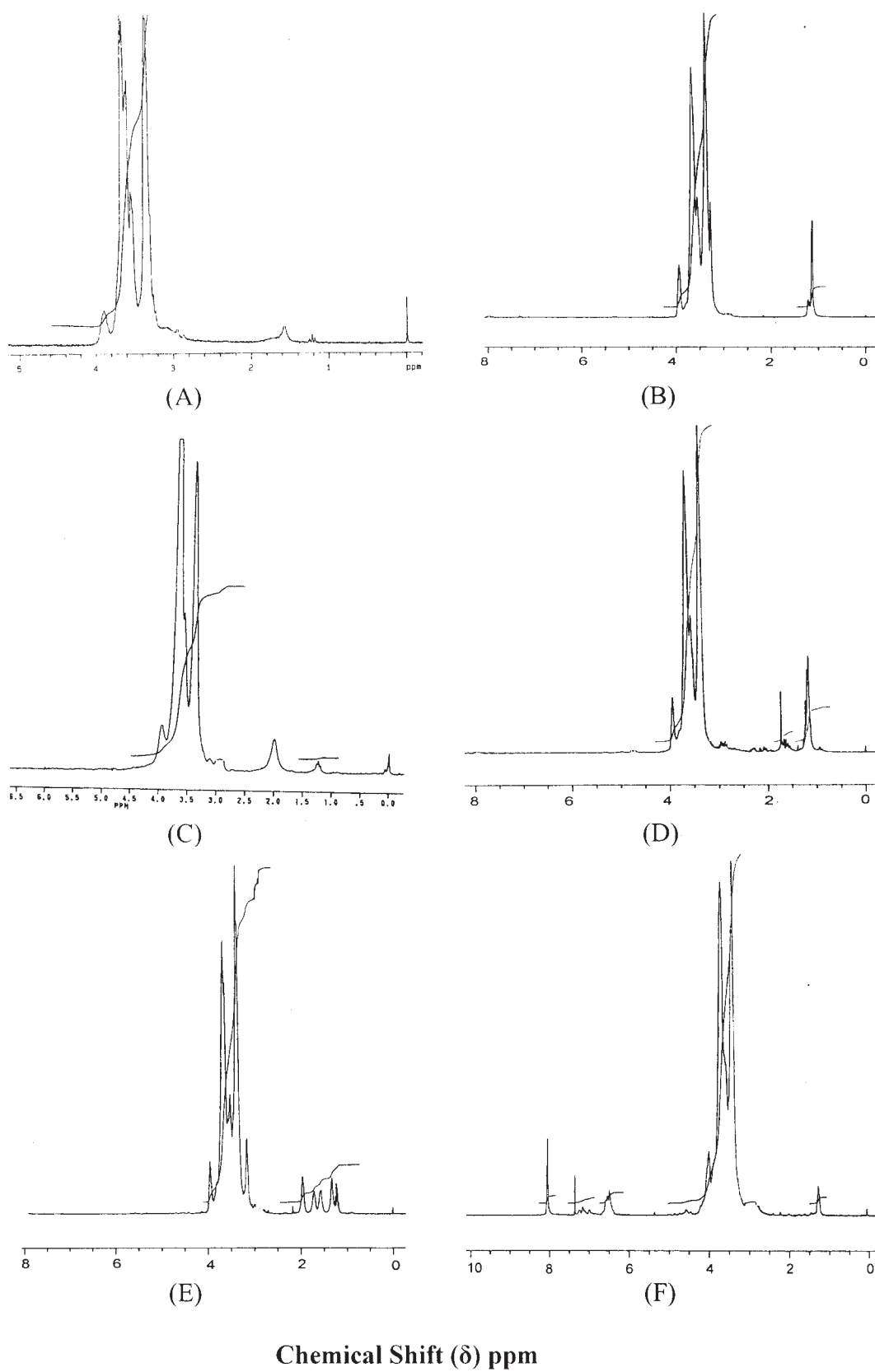


Figure 5 $^1\text{H-NMR}$ spectra of glycidyl azide polymers: (A) GAP EG; (B) GAP PD; (C) GAP DEG; (D) GAP HG; (E) GAP CHD; (F) GAP RS.

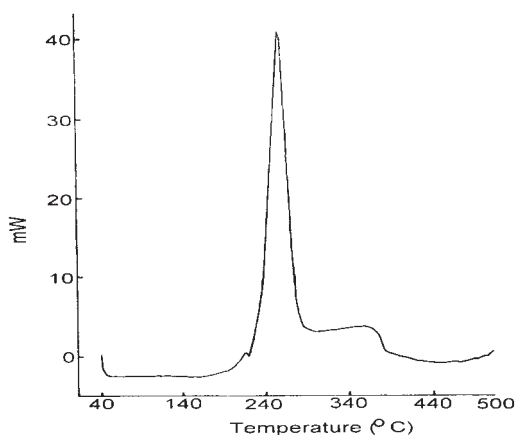


Figure 6 DSC thermogram of GAP CHD.

mic peak was observed between 240 and 255°C in all the DSC thermograms of the polymers,²⁷ which is mainly ascribed to the elimination of nitrogen by the scission of the azide bonds from the azide pendent groups of the glycidyl azide polymers.^{2,3,9,27} The thermogram of GAP (CHD) is shown in Figure 6. On closer inspection of the DSC results, a significant difference appears in the decomposition temperatures of the azide pendent group (T_{azd}) of the polymers. This is attributed to the presence of different initiative diol units in the polymer chain. The GAPs containing linear diol units (PD, DEG, HG) have lower decomposition temperatures than those containing aromatic or cyclic diols. This behavior can be explained as the diol units, other than ethylene glycol, have a flexible nature and the same characteristic is responsible for the lower decomposition temperatures of the azide pendent groups attributed to the increased flexibility of the pendent groups as a core unit of the diol in the polymer chains. The sequence of T_{azd} of the GAPs is GAP RS > GAP CHD > GAP HG > GAP DEG > GAP PD > GAP EG.

Furthermore, the decomposition temperature of the main polyether chain (T_{mcd}) is also influenced by the diol units present in the polymer chains. The linear diol units decrease the decomposition temperature of the polyether main chain but, in the case of cyclic and aromatic diol moieties, the decomposition temperature of the polymers is substantially increased. The presence of cyclic and aromatic diol moieties results in a restriction in the mobility of the polymer main chains after decomposition of the azide pendent groups. It is clearly noted that the diol units in the polymer chains are responsible not only for decreasing the azide decomposition temperatures but also for increasing the decomposition of the main polyether chain of the glycidyl azide polymers.

Fundamentally, a low glass-transition temperature (T_g) is an indication of the superior physicochemical properties of any propellant binder.¹ Because of this, the T_g values of the diol-containing GAPs were determined. The DSC curve of GAP (CHD) is shown in Figure 7. The DSC curves suggest that the GAPs containing different diol units have lower glass-transition temperatures than those of GAPs containing EG units. The complete thermal analysis of the polymers is detailed in Table II.

CONCLUSIONS

A special category series of glycidyl azide polymers, containing different diol units, were prepared by conventional method by treating the corresponding poly(epichlorohydrin)s with sodium azide. The glycidyl azide formation and diol unit attachments were confirmed by UV, IR, and proton NMR spectral analysis. Further, the diol effect on the epichlorohydrine polymerizations was studied. The diol moieties in the polymers have a significant influence on the thermal stabilities and glass-transition temperatures of the polymers. This new class of GAPs can also be used as

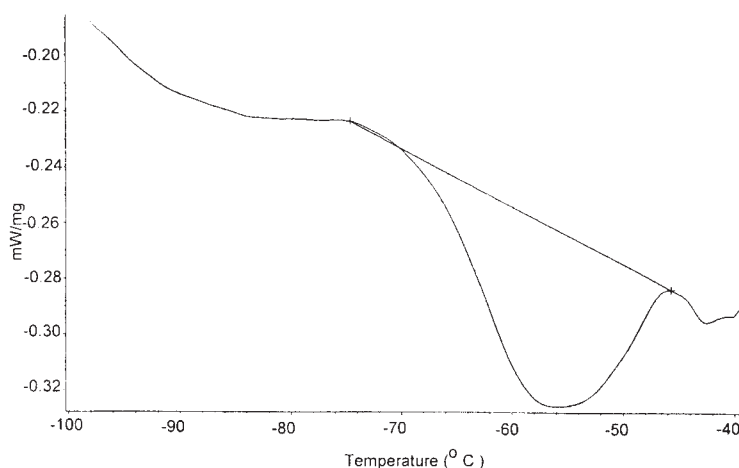


Figure 7 DSC curve of GAP DEG.

TABLE II
DSC Analysis of Glycidyl Azide Polymers

Polymer code	Decomposition temperature of azide groups in polymer (T_{azd}) (°C)	Decomposition temperature of polyether chain in polymer (T_{mcd}) (°C)	Glass-transition temperature of polymer (T_g) (°C)
GAP EG	242.70 ^a	—	-48.0
GAP PD	249.57	380.62	-66.1
GAP DEG	250.15	374.56	-66.0
GAP HG	250.86	374.35	-66.0
GAP CHD	251.33	373.11	ND ^b
GAP RS	251.95	398.22	-65.7

^a Ref. 27.

^b ND, not determined.

propellant binders or plasticizers because they showed somewhat lower glass-transition temperatures compared to that of conventional GAP.

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