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## Synthesis and Characterization of GAP-PEG Copolymers

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*A series of glycidylazide–poly(ethylene glycol) (GAP-PEG) copolymers were synthesized by cationic ring-opening polymerization of epichlorohydrin (ECH) in the presence of poly(ethylene glycol) (PEG) using borontrifluoride etherate ( $\text{BF}_3$ -etherate) as catalyst, followed by the conversion of the  $\text{CH}_2\text{Cl}$  groups of poly(epichlorohydrin) (PECH) to  $\text{CH}_2\text{N}_3$  groups. The formation of PECH-b-PEG-b-PECH triblock copolymers was confirmed by IR,  $^1\text{H}$  NMR, and  $^{13}\text{C}$  NMR spectroscopy. The corresponding GAP-b-PEG-b-GAP triblock copolymers were characterized by UV, IR,  $^1\text{H}$  NMR, and  $^{13}\text{C}$  NMR spectroscopy. The copolymers have shown an increment in their molecular weights as the higher analogue molecular weight PEGs were used in the polymerizations. The thermogravimetry-differential thermogravimetry (TG-DTG) and differential scanning calorimetry (DSC) studies of the GAP triblock copolymers indicate an increase in the decomposition temperature of the azide groups of GAP block in the copolymers caused by the introduction of higher molecular weight PEG blocks. GAP-PEG copolymers have shown lower glass transition temperatures than the homo glycidylazide polymer. The nitrogen content of the GAP-PEG copolymers was estimated by various methods and the value was in good agreement with the estimated values.*

**Keywords:** glycidylazide polymer or poly(glycidylazide), poly(ethylene glycol), ring-opening polymerization, thermal decomposition

## INTRODUCTION

Polymeric materials are playing a pivotal role in all areas, including in space technology as propellant binders, plasticizers, additives, and so

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on [1–2]. Polymeric binders whose applications are originally restricted for solid propellants are only now being employed in other explosive systems like plastic bonded explosives and gun propellants. Telechelic polymers such as carboxyl terminated poly(butadiene) (CTPB), hydroxyl terminated poly(butadiene) (HTPB), glycidyl azide polymer (GAP), and so on, are crosslinked with isocyanates to form three-dimensional network structures as desired for propellant binders [1,3–5].

During the last two decades, new promising materials have been developed, containing azido, or azidomethyl groups as energetic materials, such as glycidylazide polymer (GAP) [6–10], poly(3-azidomethyl, 3-methyloxetane)(AMMO), poly[3,3-bis(azidomethyl)oxetane](BAMO), poly(3-nitrato-methyl-3-methyloxetane) (NMMO), and its copolymers. However, the GAP is most widely used as a material for propellant binder as well as plasticizer because of its excellent properties [9]. Glycidylazide polymer is usually used as propellant binder in order to increase the burning rate, specific impulse of the propellant systems [11], and because it produces chlorine-free low pollution propellant with ammonium nitrate [12]. In fact, GAP has excellent properties like high positive heat of formation, lower density than other propellant binders, and compatibility with high energetic oxidizers [11,13]. Therefore, GAP is generally used as co-binder or as a plasticizer with hydroxyl terminated poly(butadiene) (HTPB). Due to the incompatibility of HTPB and GAP, their blended propellant may result in poor mechanical properties and performance characteristics [14–15]. It is noted that the critical temperature ( $T_c$ ) of GAP is 6°C where the binder starts to lose its elastomeric properties under the operation conditions. The plasticization process is also limited in improving the low temperature properties and processability of the GAP [14]. A facile way to improve its binder characteristics is to copolymerize it with flexible molecules. The copolymerization of GAP with vinyl and/or flexible monomers may solve these problems to some extent and currently this type of research work is going on in the authors' laboratory.

GAP and PEG propellant binders with bis-2,2 dinitropropyl acetol (BDNPA) and bis-2,2-dinitropropyl formal (BDNPF) plasticizers were studied by Shen and Leu [16]. In their study it was found that BDNPA/BDNPF were more compatible with GAP than with PEG. They also noticed that there were no changes in the thermal decomposition of GAP when BDNPA/BDNPF were used.

In contrast, the present work describes the synthesis of glycidylazide copolymer with poly (ethylene glycol) (PEG) in order to improve the low temperature properties of the GAP as well as to improve the

compatibility of the PEG binder with the BDNPA/BDNPF system. The copolymer structural elucidation, elemental analyses, molecular weight determination, and thermal properties were studied in the present investigation.

## EXPERIMENTAL

### Materials

Commercially available polyethylene glycols, such as PEG-200, PEG-400, and PEG-600, were dried over sodium sulphate for 2 days and kept over 4 Å molecular sieves. Epichlorohydrin (ECH) and methylene chloride were purified by normal distillation and borontrifluoride etherate ( $\text{BF}_3$ -etherate), and dimethylformamide (DMF) were distilled under reduced pressure. All reagents and solvents were kept under nitrogen atmosphere. Sodium azide ( $\text{NaN}_3$ ) having purity >98% was used as received. All chemicals were purchased from S.D. Fine Chemicals, Bombay. The nitrogen gas was purified by passing through pyrogallol solution and calcium chloride tower.

### Instrumentation

UV spectra of the copolymers were measured with a Shimadzu 160 A UV spectrophotometer using low concentration polymer solutions (chloroform) (1 mg/1 ml). IR spectra of the copolymers were measured with a Perkin Elmer 882 IR spectrophotometer.  $^1\text{H}$  NMR spectra of the copolymers were measured using a JEOL DELTA2-NMR 500 MHz, and  $^{13}\text{C}$  NMR spectra of the copolymers were measured, using AMX 400 spectrometer, in  $\text{CDCl}_3$  solvent using tetramethylsilane as internal standard. The DSC analysis of the copolymers was performed by an NETZSCH DSC 204 instrument with a heating rate of  $10^\circ\text{C}/\text{min}$ , under nitrogen flow. TG-DTG analysis of the copolymers was performed using ZETZSCH-Geratebau GmbH STA 409 C thermal analyzer, with a heating rate of  $10^\circ\text{C}$  under nitrogen atmosphere. The molecular weight measurements were carried out with a Waters PSS Win GPC Scientific using RI as detector and PMMA standards.

### Synthesis of PECH-PEG Copolymers [17]

The synthesis of triblock copolymers was carried out in a three-necked round bottom flask connected to a nitrogen inlet, a calcium chloride guard tube, and an efficient magnetic bar. In a typical reaction, 7.564 gms of PEG-200 was dissolved in 100 ml of chloroform and

placed in the flask. Then, 0.8 ml of borontrifluoride etherate was introduced and stirred for 30 min. To this mixture, 29.585 gms of epichlorohydrin dissolved in 50 ml of chloroform was added dropwise during 30–60 min. The reaction was carried out at 0°C for 6 h and left overnight under stirring at room temperature. Then the reaction was quenched with 50 ml of distilled water. The copolymer obtained was purified by washing with distilled water in order to remove the traces of initiator and unreacted PEG. The solvent and the unreacted monomer were removed by vacuum distillation. In all the polymerization reactions, The PEG to ECH ratio was maintained at 1:10.

### Preparation of GAP-PEG Copolymers

It is easy to convert the halogenic polyethers into the corresponding azido derivatives in aprotic solvents such as dimethylformamide (DMF), dimethyl acetamide (DMAc), and dimethylsulphoxide (DMSO), by reaction with sodium azide [18–20]. In a typical reaction, 10 gms of the PECH-b-PEG-b-PECH copolymer dissolved in dimethylformamide 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 up to 110°C in an oil bath, and then 10 gms of sodium azide was slowly added to the reaction mixture. The azidation reaction was continued for about 10 h at this temperature. Then, the mixture was cooled to room temperature and purified as per the procedure given in reference [8].

## RESULTS AND DISCUSSION

Like ethylene glycol (EG), 1,4-butanediol (BD) and other low molecular weight diols, HTPB [21–22], 4,4<sup>1</sup>-azobis(4-cyanopentanol) (ACP) [23], the poly(ethylene glycol)s (PEG)s also effectively serve as co-initiators in the ring-opening polymerization of epichlorohydrin in the presence of borontrifluoride etherate [17,23–25] to form triblock copolymer of PEG and PECH following the activated monomer mechanism [26]. In these polymerizations the monomer to diol ratio is kept at a constant value of 10 only in order to control the formation of cyclic oligomers. Cyclic oligomers may form as monomer to diol ratio increases by following the activated chain-end monomer mechanism (ACM) in addition to activated monomer mechanism (AMM).

In the present investigation, poly(ethylene glycol)s of several molecular weights were chosen as co-catalysts for the ring-opening polymerization reaction of epichlorohydrin. All the polymerizations were carried out in the presence of borontrifluoride etherate as catalyst.

**TABLE 1** Synthetic Details of PECH-PEG-PECH Copolymers

S.No.	Glycol	Amount of glycol (g)	Amount of epichlorohydrin (g)	PECH-PEG copolymer Yield (%) <sup>a</sup>	Functionality <sup>b</sup>
1	PEG-200	7.564	35.00	74.48	1.92
2	PEG-400	15.128	35.00	72.62	1.86
3	PEG-600	22.692	35.00	69.42	1.78

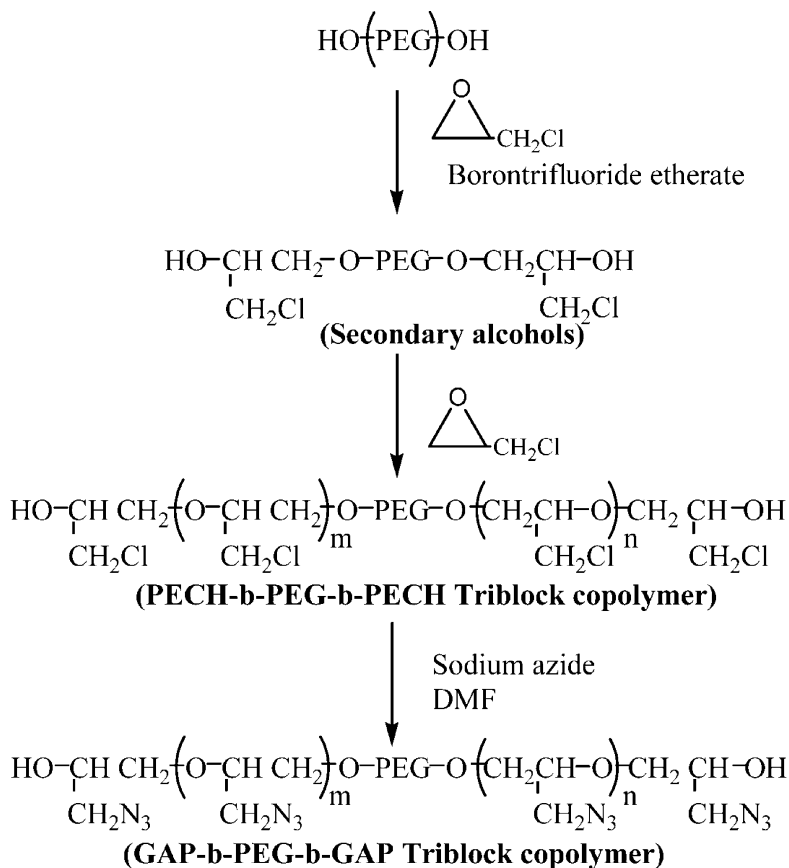
<sup>a</sup>copolymer yield = [copolymer weight / (weight of glycol + weight of epichlorohydrin)] × 100.

<sup>b</sup>functionality =  $[M_n(\text{Determined by VPO}) / (\text{Equivalent weight of copolymer})]$ .

The polymers obtained in this process have PEG blocks in the center of the chain and the PECH blocks on both ends, and have the representative copolymer structure, PECH-b-PEG-b-PECH. All the PECH-b-PEG-b-PECH copolymers were converted into their corresponding azidated copolymers, such as GAP-b-PEG-b-GAP triblock copolymers. The azidation reaction of PECH-PEG copolymers was achieved by reacting with  $\text{NaN}_3$  for 10 h at  $110^\circ\text{C}$ , because the azidation reaction was not complete at  $100^\circ\text{C}$  even after 10–11 h of reaction as reported in the literature [27]. All the copolymers were well characterized from their spectral, thermal, and elemental analysis. It was found that there was no effect on the azidation reaction either by molecular weight or by the hydroxyl groups present in the copolymer [28]. The GAP-PEG copolymers synthesized were found to have number average molecular weights between 1100–1600 as determined by VPO, and the molecular weights of the copolymers have increased along with the PEG molecular weights chosen for the polymerization. The synthetic details of the PECH-PEG copolymers are given in Table 1. A typical schematic representation of the preparation of GAP-PEG copolymer is shown in Scheme 1.

## Molecular Weight

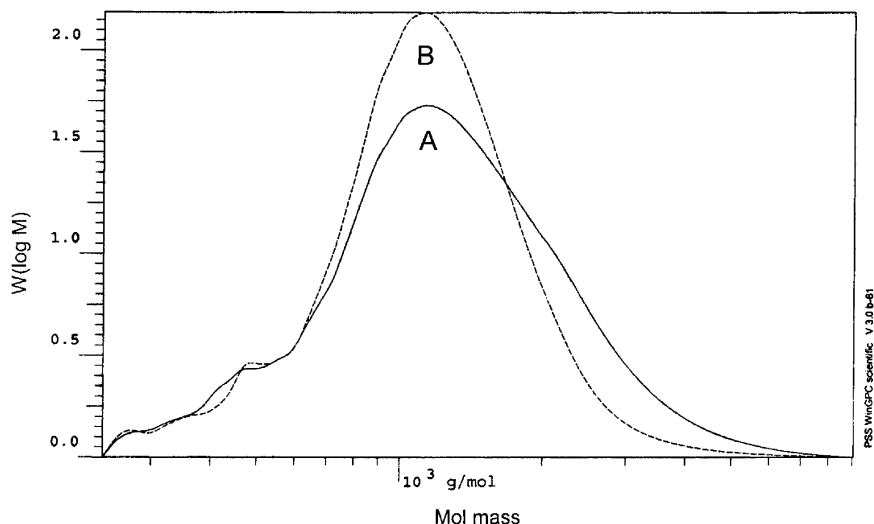
The average molecular weights of the copolyethers synthesized in this investigation by using PEG/ $\text{BF}_3$ -etherate initiating system have shown to be low due to the restriction of the monomer to diol ratio. The number average molecular weights of the PECH-PEG copolymers and GAP-PEG copolymers are given in Table 2. The relative measure of the number average molecular weight of the copolymers is increased as PEG higher of molecular weight was used in the polymerization. In the azidation reaction of PECH-PEG copolymers with sodium azide, all the chlorine atoms are replaced by azide groups, which leads to



**SCHEME 1** Schematic representation of the preparation of GAP-PEG copolymer.

**TABLE 2** Molecular Weight Data of PECH-PEG and GAP-PEG Copolymers

Copolymer code	VPO (Mn)	GPC (Mn)	GPC (Mw)	Polydispersity (Dp)
PECH-PEG(200)	1056	975	1242	1.27
PECH-PEG(400)	1185	997	1371	1.37
PECH-PEG(600)	1290	1028	1486	1.44
GAP-PEG(200)	1193	1034	1397	1.35
GAP-PEG(400)	1345	1167	1579	1.35
GAP-PEG(600)	1482	1242	1695	1.36



**FIGURE 1** GPC curves of (A) PECH-PEG(200)-PECH and (B) GAP-PEG(200)-GAP copolymers.

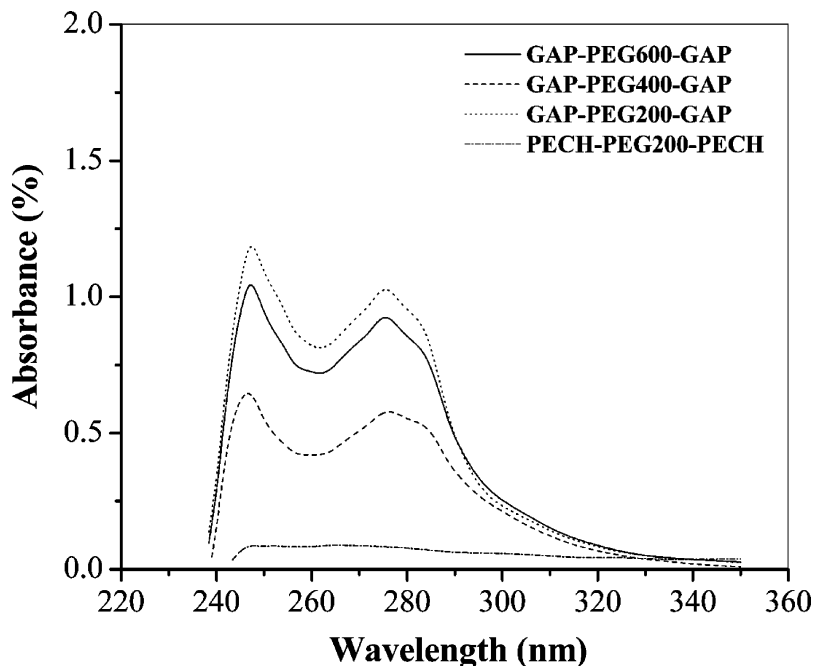
increment in the copolymer molecular weight. This shows that there is no effect of the azidation reaction on the molecular weight of the copolymer and on its hydroxyl groups [28]. Higher molecular weight or branched PECH [10] azidation reactions may lead to decrement in molecular weight in the presence of base, caused by the degradation of the PECH chains in the azidation reaction. The GPC molecular weight curve of PECH-PEG(200)-PECH and GAP-PEG(200)-GAP is shown in Figure 1.

### Spectral Analysis

The PECH-PEG copolymers and the corresponding azidated copolymers (GAP-PEG) are well characterized from their UV, IR,  $^1\text{H-NMR}$ , and  $^{13}\text{C-NMR}$  spectral analysis [23,29]. The UV spectra of PECH-PEG-PECH and GAP-PEG-GAP copolymers are presented in Figure 2. The UV spectra of GAP triblock copolymers shows two absorption peaks at 248 nm and 278 nm corresponding to the resonance of nitrogen bonds of the azide group of the GAP block of the triblock copolymers [9,28–29], whereas their precursor PECH-PEG-PECH copolymers do not show any absorbance in this region [9,29].

The IR spectra of the PECH-PEG-PECH triblock copolymers have shown the main characteristic peaks around  $745\text{ cm}^{-1}$  ( $-\text{CH}_2\text{Cl}$ ),

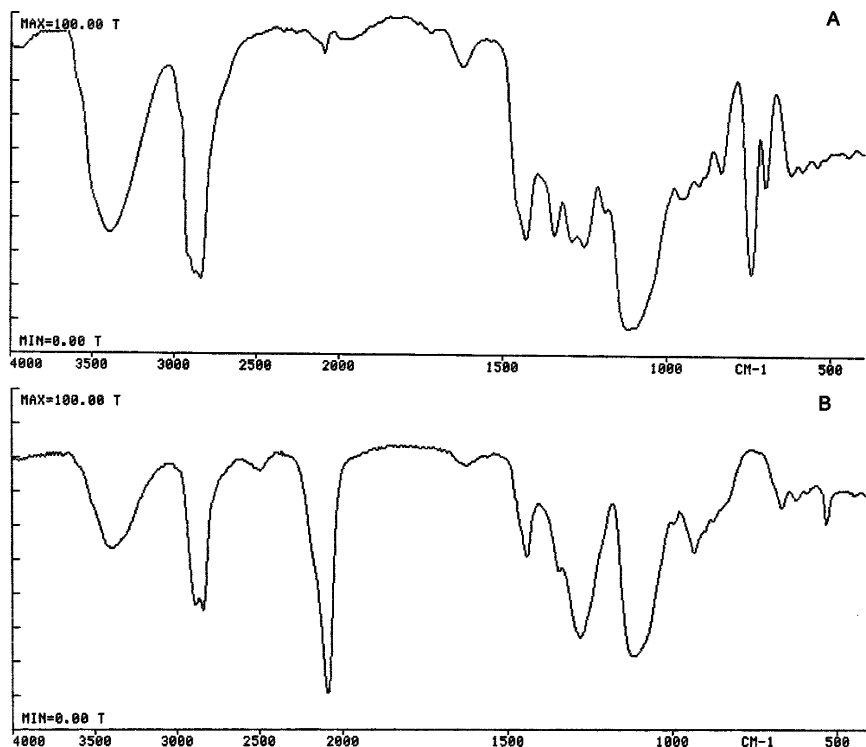




**FIGURE 2** UV spectra of the PECH-PEG-PECH and GAP-PEG-GAP copolymers.

1190  $\text{cm}^{-1}$  (C–O–C), 2845  $\text{cm}^{-1}$  (–CH, –CH<sub>2</sub>), and 3380  $\text{cm}^{-1}$  (–OH) [9,29–31]. The formation of azide groups in the triblock copolymers GAP-PEG-GAPs is clearly demonstrated from their IR studies. The IR spectra of the GAP-PEG-GAP copolymers indicate the complete disappearance of the CH<sub>2</sub>Cl peak at 745  $\text{cm}^{-1}$  and subsequent formation of a strong peak at 2080  $\text{cm}^{-1}$  corresponding to the azide group, confirming the complete replacement of chlorine atoms by azide groups in the PECH block of the copolymers [9,30]. The IR spectra of PECH-PEG(200)-PECH and GAP-PEG(200)-GAP copolymers are presented in Figure 3.

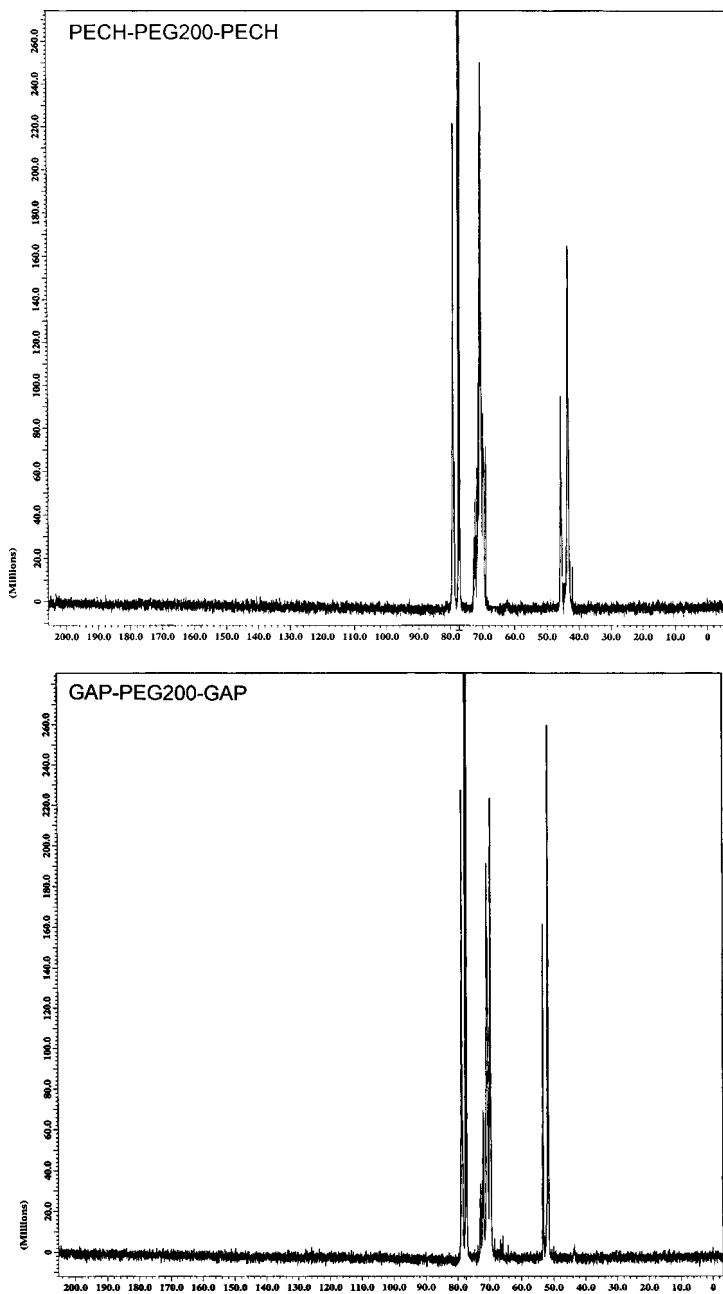
The <sup>1</sup>H-NMR and <sup>13</sup>C-NMR spectral analysis also supports the formation of copolymers [29]. In the <sup>1</sup>H NMR spectra of PECH-PEG-PECH copolymers, peaks are observed at 3.4 ppm due to CH<sub>2</sub>Cl protons of the pendant PECH block, and at 3.8 ppm due to the protons of CH<sub>2</sub>, CH groups of the polyether main chain of PECH and CH<sub>2</sub> protons of PEG block. The <sup>1</sup>H-NMR spectra of GAP-PEG-GAP copolymers, show peaks at 3.25 ppm assigned to methylene protons of the



**FIGURE 3** IR spectra of (A) PECH-PEG(200)-PECH and (B) GAP-PEG(200)-GAP copolymers.

pendant azidomethyl groups ( $-\text{CH}_2\text{N}_3$ ) of GAP and at 3.4–3.8 ppm assigned to the main chain methylene protons of GAP, PEG blocks, and CH protons of GAP block. In the  $^{13}\text{C}$ -NMR spectra of the PECH-PEG-PECH copolymers, the chloromethyl carbon peaks are seen as a pair of peaks at 42–47 ppm, the strong methylene carbon resonance peaks of the PECH and PEG are visible at 70.00 ppm, and the peaks corresponding to CH signals of PECH are present at 80.00 ppm. This further confirms the formation of PECH-PEG-PECH copolymers. The  $^{13}\text{C}$ -NMR spectra of the GAP-PEG-GAP copolymers show the azidomethyl carbon signals of GAP block at 52–54 ppm and the complete disappearance of the resonance signals at 42–47 ppm, confirming the completion of azidation reaction. The  $^{13}\text{C}$ -NMR spectra of the PECH-PEG(200)-PECH and GAP-PEG(200)-GAP are presented in Figure 4.

From the earlier spectral analysis, the formation of the PECH-PEG-PECH copolymers by the ring opening polymerization is clearly



**FIGURE 4**  $^{13}\text{C}$ -NMR spectra of PECH-PEG(200)-PECH and GAP-PEG(200)-GAP copolymers.

demonstrated, and further completion of the azidation reaction to form GAP-PEG-GAP copolymers. Furthermore, the spectral analysis clearly demonstrates the presence of PECH and PEG in PECH-PEG-PECH copolymers and GAP and PEG blocks in GAP-PEG-GAP copolymers, along with the terminal hydroxy end groups.

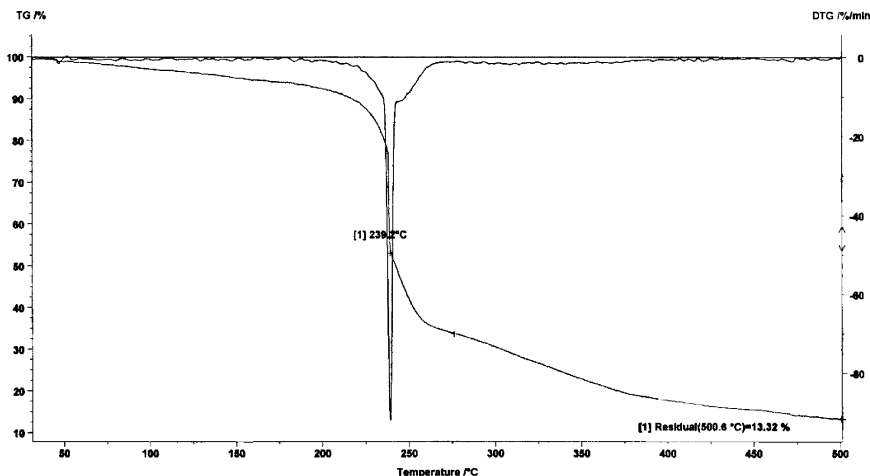
## Thermal Studies

### *Decomposition Studies*

It is essential to study the decomposition behavior of polymeric propellant materials, if they are going to be used in space technology applications because the polymeric propellant binders play a crucial role in the combustion behavior of the composite solid propellants. Therefore, decomposition studies of the synthesized GAP-PEG-GAP copolymers were performed using TG-DTG and DSC.

In addition to the already above discussed spectroscopic analysis, thermal analysis techniques are employed to characterize the GAP-PEG copolymers [9,30]. In the TG-DTG analysis of GAP-PEG copolymers, a two-step degradation behavior is observed. The first step starts around 180°C and the second starts around 290°C. These degradation steps are due to the nitrogen elimination from the azide group of the GAP units in the copolymers and the degradation of the polyether main chain of the GAP and PEG units, respectively [11]. A slight variation is observed in the peak decomposition temperature ( $T_d$ ) of GAP block in the copolymer thermograms. The increment in their maximum decomposition temperature is mainly due to the presence of PEG blocks in the copolymer. The reason for increment in the  $T_d$  values is the hindrance of PEG blocks on the azido groups of GAP in the copolymer. A representative DTG-TG curve of GAP-PEG(200)-GAP copolymer is presented in Figure 5.

From the DSC curves, it is noticed that there are no decomposition signals for the GAP-PEG-GAP copolymers below 160°C. However, the onset of decomposition of the copolymers is observed around 160–167°C. A GAP-PEG(200)-GAP copolymer DSC curve is depicted in Figure 6. A strong single exothermic peak in all the DSC curves of the GAP-PEG-GAP copolymers is found between 252–271°C, similar to glycidyl azide polymer [9,30–31]. This decomposition is due to the elimination of nitrogen molecules by the scission of the azide bonds from the azide pendant groups of the GAP block of the copolymer [11]. The variation in the decomposition behavior of the copolymers is clearly apparent as the PEG block varied. The peak decomposition temperature of the copolymers increases as the molecular weight of the PEG block molecular weight increases. This increment in peak



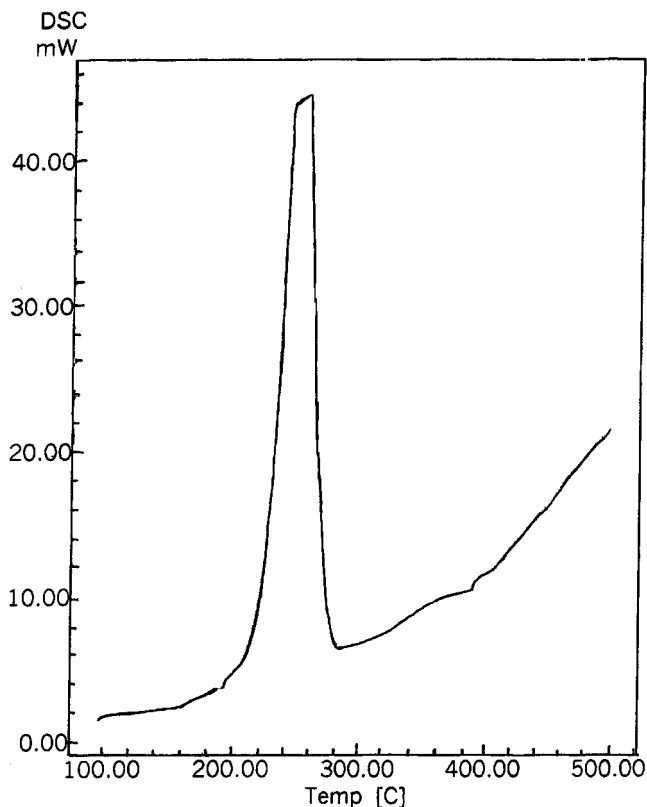
**FIGURE 5** DTG-TG thermogram of GAP-PEG(200)-GAP copolymer.

decomposition temperature is due to a decreasing number of azido units of GAP in the copolymer.

Moreover, the exothermic behavior of the GAP-PEG-GAP copolymers can be explained from their heat of decomposition exotherm values ( $\Delta H$ ) [9]. These decomposition values are high for the copolymers containing low molecular weight PEG blocks, because they contain a higher number of azide groups that are responsible for higher amount of heat release. As the molecular weight of the PEG block increases in the copolymer their decomposition exotherm values decreased. Full results of all the thermal studies are tabulated in Table 3.

### **Glass Transition Temperature**

The authors have determined the glass transition temperatures ( $T_g$ ) of the copolymers, because the GAP is suffering from inferior low temperature mechanical properties due to somewhat higher  $T_g$ . The GAP-PEG-GAP triblock copolymers have showed very low glass transition temperatures, like glycidylazide-ethylene oxide (GAP-EO) copolymer, branched GAP, low molecular weight GAP, and its copolymer [32–34]. The copolymers have showed much lower  $T_g$  values than GAP itself. The flexible groups of the PEG block in the copolymers have reduced the glass transition temperature of the copolymers to below GAP. This behavior of the copolymers is a gradual process. As the molecular weight of the PEG block of the copolymer increases the  $T_g$  of the corresponding copolymer decreases to lower temperatures.

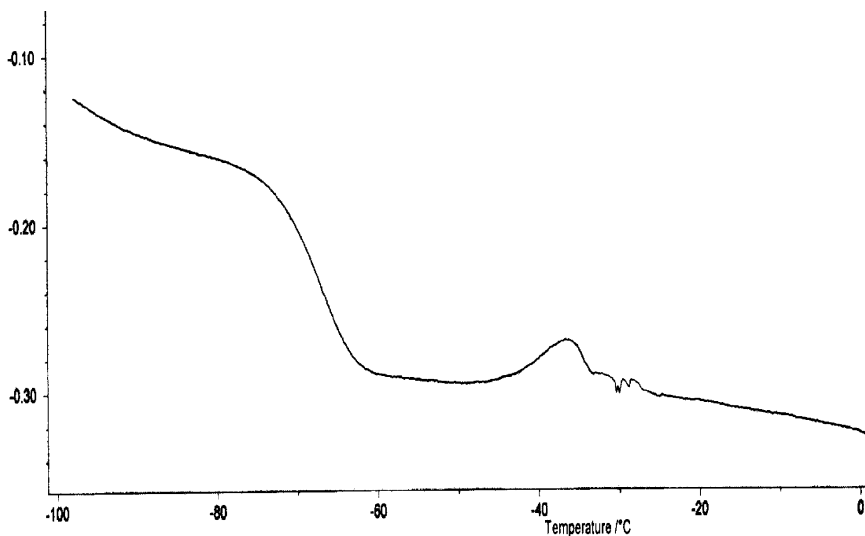


**FIGURE 6** DSC curve of GAP-PEG(200)-GAP copolymer.

Furthermore, these copolymers have a single glass transition temperature, between the two  $T_g$  values of their corresponding homopolymers. The single  $T_g$  of the copolymer indicates that there is compatibility between the GAP and PEG blocks in the copolymer.

**TABLE 3** Thermal Properties of GAP-PEG Copolymers

Copolymer	DSC results						DTG-TG results
	$T_g$ (°C)	$T_0$ (°C)	$T_{\text{exon}}$ (°C)	$T_d$ (°C)	$T_f$ (°C)	Energy (J/g)	$T_d$ (°C)
GAP-PEG(200)	-63	162	208	252	284	1510	239.2
GAP-PEG(400)	-68	164	209	263	293	1230	243.5
GAP-PEG(600)	-72	167	209	271	294	1054	247.6



**FIGURE 7** DSC glass transition temperature curve of GAP-PEG(600)-GAP copolymer.

A representative DSC  $T_g$  curve of GAP-PEG(600)-GAP copolymer is shown in Figure 7.

### **Nitrogen Content in the Copolymers**

The nitrogen elemental analysis of the GAP-PEG-GAP copolymers was performed following the redox method [35] and compared the nitrogen content with DSC studies as well as with instrumental analysis. The nitrogen content values of the copolymers are in good agreement with all the methods of analysis and the complete details are given in Table 4.

The triblock copolymers prepared in this investigation containing the hydroxyl terminal groups with GAP and PEG blocks, have lower  $T_g$  values, good compatibility between the two blocks in the copolymer, and possess high energetic azide groups as pendants on the copolymer

**TABLE 4** Nitrogen Content of GAP-PEG Copolymers

Copolymer	Instrumental analysis	Redox analysis	DSC analysis
GAP-PEG(200)	34.92	34.56	35.04
GAP-PEG(400)	28.30	29.07	28.54
GAP-PEG(600)	24.25	23.85	24.45

chains. Therefore, these triblock copolymers may find applications in rocket propellant technology as energetic polymeric propellant binders/additives.

## CONCLUSIONS

Triblock copolymers of GAP and PEG were synthesized by using various PEGs as diols in the cationic ring opening polymerization of epichlorohydrin, using borontrifluoride etherate as initiator and subsequent azidation of the copolymer with sodium azide. They were characterized by spectral methods such as UV, IR,  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR. The glass transition temperature of the copolymers is lowered as the PEG block molecular weight increases, as employed in the polymerization. The  $T_g$  of GAP-PEG triblock copolymer was considerably low, at  $-72^\circ\text{C}$ , which is significant for the utilization as a polymeric binder in the propellant technology. Furthermore, these copolymers have shown similar degradation behavior as GAP homopolymer, but the peak decomposition temperature is varied as the PEG block molecular weight varies. GAP-PEG(600)-GAP copolymer showed higher decomposition temperature than any of the copolymers and homo GAP.

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